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KINKEN Research Highlights 2021

Institute for Materials Research, Tohoku University



Research

KINKEN

Research Highlights

2021



Institute for Materials Research, Tohoku University

KINKEN Research Highlights 2021

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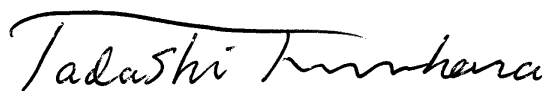
Preface

Dear Colleagues,

We are pleased to present *KINKEN* Research Highlights 2021, which is the annual report that includes a collection of research outputs of the past year from the Institute for Materials Research (IMR), Tohoku University. *KINKEN* is the abbreviation for “Kinzoku Zairyo Kenkyujo,” the Japanese name for IMR, which is well known in the materials science community.

IMR was the first Tohoku University research institute, of which there are currently six, to be established in 1916. Aiming to contribute to the well-being of the human race and the development of civilization through the creation of new materials that are useful to society, it carries out research on both the fundamentals and applications of a wide range of substances and materials. After its founding, IMR first focused on steel but quickly expanded its research area to the other metals and alloys. Then, in response to changing times and economic growth, it came to cover semiconductors, ceramics, and a wide range of other materials. Ever since our first director, Professor Kotaro Honda, invented the first artificial permanent magnet called “KS steel,” we have developed many new materials for practical use, including Sendust alloy, SiC fibers, and soft magnetic amorphous alloys. We have also focused on fundamental research, which is important for the development of new materials, as well as carried out cutting-edge research on magnetism, optical properties, superconductivity, and microstructure of materials. While doing so, IMR has become a leading research institute in the field of materials science.

IMR is notable for its fusion of fundamental and applied research, as well as of science and engineering. We offer some of the best large research facilities in the world — covering high-energy



Director Prof. Tadashi Furuhashi



irradiation, strong magnetic fields, and supercomputing — enabling researchers from Japan and abroad to engage in a variety of collaborative projects. To develop superior or new materials that are useful, we believe it is necessary to organically connect three “pillars”: (1) the “exploration” of physical phenomena that govern materials’ functions, (2) the “creation” of materials via various methods, and (3) the “measurement” of materials’ properties from various perspectives. IMR has for many years been contributing to the materials research community via our joint usage/research programs. IMR celebrated its 100-year anniversary in 2016. Having been designated in 2018 as an International Joint Usage/Research Center in Materials Science, known as Global Institute for Materials Research Tohoku (GIMRT), we have now further heightened our efforts to enhance such collaborations and cultivate new talent.

In the 21st century, our society faces global-scale environmental issues, such as global warming, resource depletion, acquiring a stable energy supply, and new kinds of environmental pollution. IMR will continue to work towards a sustainable society both by engaging in important research to solve various problems as well as by creating new areas of research that can bring about paradigm shifts in the future.

We hope that the KINKEN Research Highlights will enable you to better understand our recent research activities and will aid the promotion of worldwide collaboration with IMR. We ask for your continued support and welcome any suggestions.

Infrastructural Materials

IMR KINKEN Research Highlights 2021



Interaction of Alloying Element with Migrating Ferrite/Austenite Interface in Phase Transformation

Alloying elements significantly influence the phase transformation kinetics in steel. A quantitative understanding of alloying effects is key to tailoring the mechanical properties of modern high-strength steels. Therefore, in this study, alloying effects were quantitatively investigated, with special attention to energy dissipation during interface migration in phase transformation.

A variety of phase transformations have been utilized in microstructure design to tailor the mechanical properties of steel products. In the development of modern high-strength steel, sophisticated control of the transformation microstructure is required for improved strength and ductility-toughness balance. Therefore, a quantitative understanding of alloying effects on phase transformation kinetics in a basic Fe-C system has become increasingly important.

An alloying element can influence phase transformation kinetics by (1) changing the phase stability or (2) dynamic interaction with the migrating interface. The development of the CALPHAD method has made it possible to calculate alloying effects on phase stability. However, the effects of the latter have yet to be elucidated in detail.

Our group developed a multi-aspect characterization method to clarify the interaction between the alloying element and the interface quantitatively [1]. The method includes energy dissipation measurement based on the deviation of the interfacial carbon composition from the equilibrium using a field-emission electron probe micro-analyzer; the direct observation of alloying element distribution at the interface using a three-dimensional atom probe (3DAP); and interface crystallography characterization using electron backscatter diffraction.

Figure 1(a) shows an incoherent interface separating ferrite with a low C content (left) and austenite with a high C content (right) [1]. Mo segregation at the ferrite/austenite interface is clearly seen in Mo atom map in Fig. 1(a). The amount of Mo segregation was quantified from the composition profile across the interface shown in Fig. 1(b). Such Mo segregation resulted from the strong interaction between Mo and the interface, which dissipated energy during migration leading to transformation delay. These results are in good agreement with the theoretical model developed in this study, as shown in Fig. 1(c).

It was clarified that the interaction between the alloying element and semi-coherent interface was significantly weaker than that at the incoherent interface, which induced remarkably different alloying effects on displacive transformation, e.g., bainite transformation [2]. It was also found that transformation strain caused energy

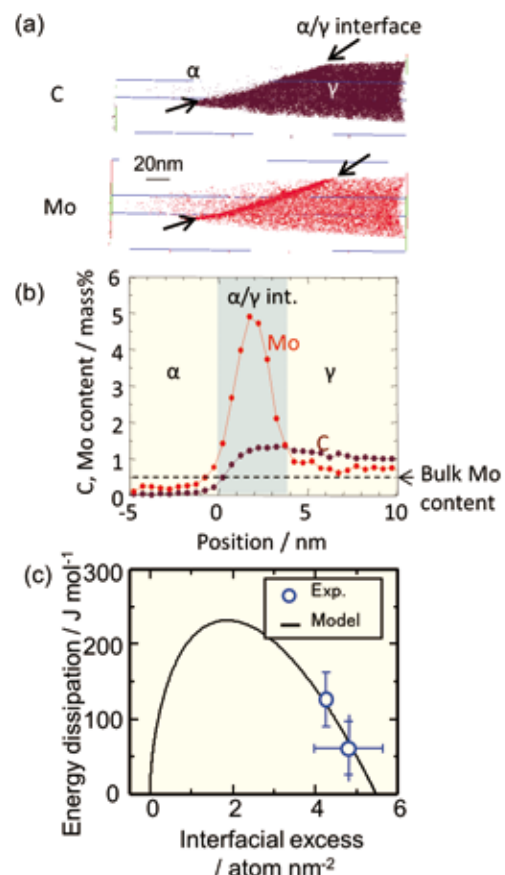


Fig. 1 (a) C and Mo atom map at the α/γ interface measured using 3DAP in the Fe-0.5Mo-0.4C alloy transformed at 973 K for 600 s. (b) C and Mo composition profile obtained perpendicular to the α/γ interface in (a). (c) Relation between the amount of Mo segregation (interfacial excess) and energy dissipation compared with the model calculation [1].

dissipation during migration of the semi-coherent ferrite/austenite interface even in a Fe-C binary alloy [3].

References

- [1] G. Miyamoto, K. Yokoyama, and T. Furuhashi, *Acta Mater.* **177**, 187 (2019).
- [2] G. Miyamoto and T. Furuhashi, *ISIJ Int.* **60**, 2942 (2020).
- [3] H. Dong, Y. Zhang, G. Miyamoto, Z. Yang, and T. Furuhashi, *Scr. Mater.* **188**, 59 (2020).

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Dislocation Motion After Hydrogen Charging Characterized by In Situ Electron Channeling Contrast Imaging

Hydrogen contributes to the plasticity-induced cracking of metallic materials. In particular, the interactions between hydrogen, dislocations, and grain boundaries have been studied to understand the hydrogen-assisted cracking mechanism. Therefore, a visualization technique for dislocation motion interaction with hydrogen near grain boundaries is required. We successfully applied in situ scanning electron microscopy to observe the dislocation motion in a hydrogen-charged metallic bulk specimen.

Hydrogen-dislocation interactions in metals have been recognized as the most crucial factor that triggers hydrogen embrittlement. Therefore, the visualization of dislocation motion under the influence of hydrogen may be the key to understanding the underlying mechanism of hydrogen embrittlement. However, there are two challenges in observing the dislocation motion with the hydrogen effect: (1) hydrogen can be desorbed and diffused easily even at room temperature; (2) the hydrogen-dislocation interaction suffers from the thin film effect. Therefore, to characterize the hydrogen-related phenomenon, a dislocation-resolved and kinetically resolved method must be used with a bulk specimen. In this context, we applied in situ electron channeling contrast imaging (ECCI) to characterize the dislocation motion in hydrogen-charged steel. ECCI is a scanning electron microscopy (SEM)-based method. Through ECCI, we successfully observed dislocation motion after hydrogen charging in an Fe-based bulk specimen.

A schematic of the experiment is shown in Fig. 1 [1]. The mechanically polished specimen with a thickness of 1 mm was hydrogen-charged for 3 h in an aqueous solution of 5% H_2SO_4 with 3 g L^{-1} NH_4SCN (Fig. 1A, 1B). The specimen surface was then repolished to remove the contaminants that formed during hydrogen charging (Fig. 1C). The polished surface was observed by ECCI (Fig. 1D), which visualized the dislocation motion at different times (Fig. 1E).

The ECC images with different vacuum exposure times in the SEM are shown in Fig. 2. The dislocations, denoted as **a** to **g**, moved from the grain boundary to the grain interior. In particular, the dislocation motion became distinct after exposure for 2 h. These results indicate the following: (1) a hydrogen-related phenomenon occurred, which became significant after 2 h; and (2) there is a factor that facilitates dislocation motion from the grain boundary. According to atomistic simulations [1], the phenomenon corresponding to fact (1) is hydrogen diffusion to the grain boundary. The hydrogen localization at the grain boundary generated sufficient shear stress to trigger dislocation motion.

The hydrogen-assisted dislocation motion from the grain boundary is important for understanding plasticity-induced cracking because grain boundary cracking with hydrogen has been reported to result from dislocation motion

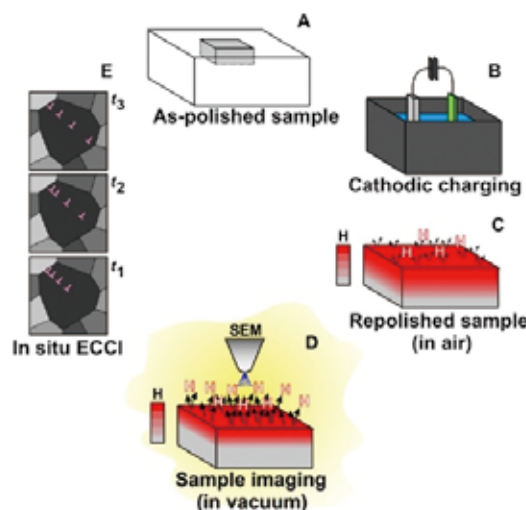


Fig. 1 Schematic illustrations of the in situ ECCI observations after hydrogen charging.

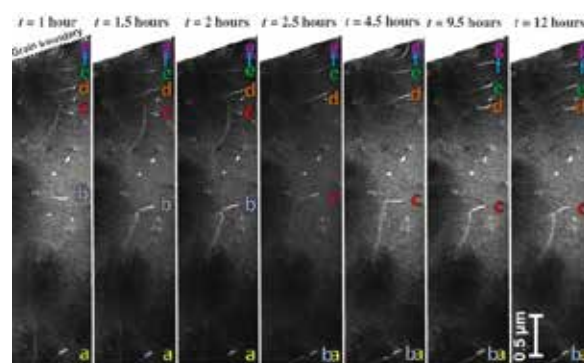


Fig. 2 Dislocation motion with different exposure times after hydrogen charging. The exposure times are indicated on the top of the images.

near the grain boundaries. The in situ ECCI technique can be performed under tensile loading. Further in situ ECCI experiments with the hydrogen effect will be carried out under tension after hydrogen charging.

References

- [1] M. Koyama, S.M. Teheri-Mousavi, H. Yan, J. Kim, B.C. Cameron, S.S. Moeini-Ardakani, J. Li, and C.C. Tasan, *Sci. Adv.* **6**, eaaz1187 (2020).

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Surface Characterization of Functional Iron-Gallium Alloys Annealed Under Different Conditions

Fe-Ga alloys are functional magnetostrictive materials that are promising for application in actuators and sensors. In this study, the surface state of Fe₈₀Ga₂₀ alloys annealed under different atmospheric conditions was characterized with X-ray absorption spectroscopy and secondary ion mass spectrometry. Through the analysis, we report selective oxidation of Ga in the Ar-10%H₂ atmosphere.

FeGa alloys are new magnetostrictive materials. They are promising as smart materials for application in actuators and sensors. Since these applications are often expected to be used outdoors, it is necessary to control the surface conditions to ensure anticorrosion. In such cases, Ga₂O₃ is formed on the surface, which is chemically more stable than Fe₂O₃. In this study [1], the surface condition of the Fe-20at%Ga (Fe₈₀Ga₂₀) alloys annealed under different conditions were investigated by X-ray absorption spectroscopy (XAS) measurements in the conversion electron yield (CEY) to elucidate the effect of the atmosphere on the surface properties of these alloys.

Buttons of Fe₈₀Ga₂₀ alloy were prepared by arc melting. The buttons were cut into discs, diameter 10 mm and thickness 1 mm. After the disk samples were polished mechanically [condition (a)], they were annealed in air at 873 K for 3600 s [condition (b)] or in Ar-10 % H₂ gas at 873 K for 3600 s [condition (c)]. Figure 1 shows the CEY-XAS spectrum for Fe₈₀Ga₂₀ samples annealed under conditions (a)-(c) and oxide standards of Fe₂O₃ and Ga₂O₃. The CEY-XAS spectrum of the Fe and Ga K absorption edge is different for the metallic state sample corresponding to condition (a) compared with that of the oxide standard. The Fe and Ga K absorption edges of the (b) are both observed between the (a) and the oxide standard. On the other hand, the Fe K absorption edge of the sample treated using (c) shows the spectrum consistent with that of (a), however, the Ga K absorption edge is located between the metal and the oxide standard. This result suggested the selective formation of Ga₂O₃ on the surface of Fe₈₀Ga₂₀ annealed under condition (c). The depth profiles of iron, gallium, and oxygen ions of Fe₈₀Ga₂₀ annealed in condition (c) measured with the TOF-SIMS technique are shown in Fig. 2. The signal intensity derived from Fe increased at the interface of the oxide layer. These results of CEY-XAS and TOF-SIMS suggested that the Fe concentration in the oxide layer is lower than

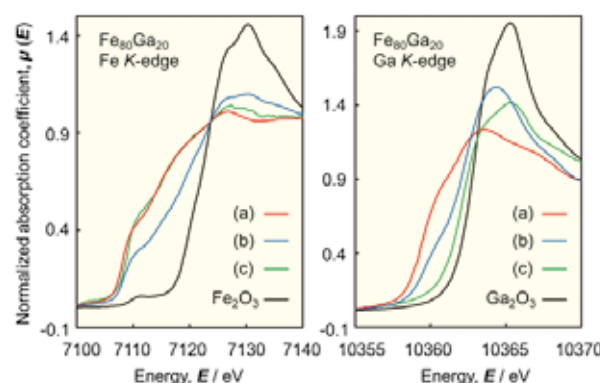


Fig. 1 CEY-XAS spectrum near of Fe and Ga K edge for Fe₈₀Ga₂₀ annealed under condition (a)-(c).

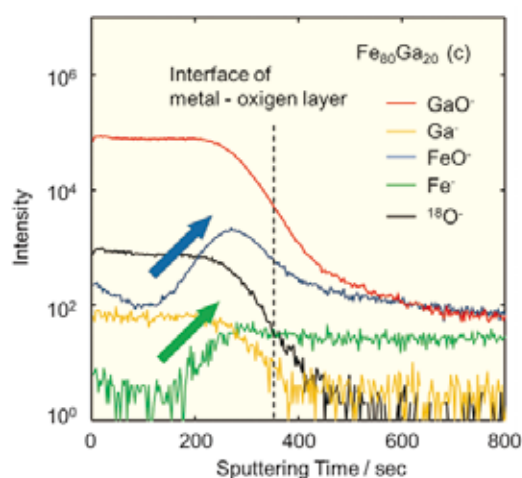


Fig. 2 Depth profiles of Fe₈₀Ga₂₀ annealed under condition (c) obtained by TOF-SIMS.

that of Ga and that heat treatments of Fe-Ga alloys under a low partial pressure of oxygen can effectively form protective or corrosion-resistant layers, which are composed of less-noble gallium oxides.

References

- [1] T. Kawamata, K. Shinoda, K. Sugiyama, and S. Suzuki, *Surf. Interface Anal.* **52**, 1098 (2020).

Keywords: surface reaction, synchrotron, XAFS

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Microstructure Refinement for Superior Ductility of Al–Si Alloy by Electron Beam Melting

Refining the microstructure to improve the ductility of cast Al–Si alloys is challenging. Recently, we reported a novel microstructure refinement approach for AlSi10Mg alloy via the synergetic effects of superheating, fast cooling, and preheating using electron beam melting (EBM) technology. A fine granular Si phase (0.5–2 μm) and bimodal Al grains (40 μm and 0.5–2 μm sub-grains) were obtained in the as-EBM-built AlSi10Mg alloy, which resulted in an improved tensile elongation exceeding 30%.

Al–Si alloys are widely applied to thin walls, complex geometries, and parts subjected to large loads because of their high corrosion resistance, weldability, and hardenability due to natural or artificial aging. Refining the Si phase is essential for improving the ductility of cast Al–Si alloys because cracks can initiate in the coarse, acicular Si phase.

The ductility improvement of as-cast Al–Si alloy by adding modification elements is limited. Previous studies have shown that reheating the Al–Si alloy to a much higher temperature than its melting point could refine both the Si phase and Al grains under a fast cooling rate. This provides a novel approach for refining the microstructure of Al–Si alloys using additive manufacturing (AM) technology.

Here, electron beam melting (EBM), an AM process, was selected to refine the AlSi10Mg alloy because of its high building temperature, fast cooling rate, and preheating process. In the as-built alloy, mixed fine island-like and scattered granular Si phase particles (approximately 2 μm) with rounded corners and edges were embedded into the Al matrix, as shown in Fig. 1 [1].

An Al matrix with a mean grain size of approximately 40 μm and fine sub-grain size of 0.5–2 μm was obtained in the as-EBM-built AlSi10Mg alloy. During the building process, the high-temperature inner melt pool (>1500 $^{\circ}\text{C}$) gave rise to a fully homogeneous Al–Si liquid in a true equilibrium solution state without undissolved Al-enriched and Si-enriched nanoparticles. Afterward, the Si and Al phases nucleated directly and grew to fine grains owing to the fast cooling rate of the inner melt pool. A high tensile elongation of approximately 33% was obtained owing to the refined microstructure of the as-EBM-built AlSi10Mg alloy.

This study provides a novel alloy manufacturing method to improve the microstructure and mechanical properties of alloys consisting of elements with significantly higher melting point differences, such as Al–Si alloy systems, using EBM technology.

References

- [1] H. Bian, K. Aoyagi, Y. Zhao, C. Maeda, T. Mouri and A. Chiba, *Addit. Manuf.*, **32**, 100982 (2020).

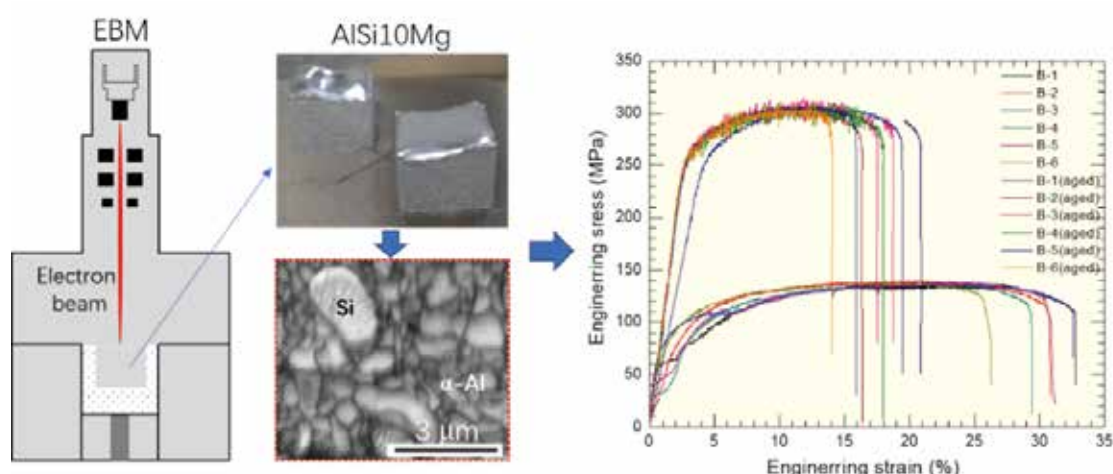


Fig. 1 The as-EBM-built AlSi10Mg alloy with fine Si and Al grains lead to high tensile ductility. After T6 aging, the tensile strength increased.

Keywords: additive manufacturing, aluminum alloys

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Hot Deformation and Recrystallization Behaviors of Medium-Entropy Alloys

Multiprincipal element alloys have attracted significant academic interest, but their hot deformation characteristics are relatively unknown. We investigated the hot deformation, dynamic recrystallization, and microstructural evolution of typical medium entropy alloys at single-phase temperatures, which provide guidelines for microstructure refinement via thermomechanical processing.

High- or medium-entropy alloys (HEAs, MEAs), which consist of multiprincipal elements, have attracted much attention because of their unusual structures and properties. However, the insufficient strength of these alloys hinders their application. To further improve their mechanical performance, a precipitation-strengthened MEA was designed by adding a strong γ' -phase former (Ti, Al) to the CoCrNi MEA [1]. However, the deformation and recrystallization behavior of the MEA at high-temperature remains unclear.

Here, we reveal the deformation behavior of typical CoCrNi and (CoCrNi)₉₆Ti₃Al₃ MEAs by hot compression at single-phase temperatures [2]. A constitutive model was constructed and the relationship between the recrystallization, strain rate, and temperature was clarified. Figure 1 shows the compressive true stress-strain curves of the two MEAs at 1173 K. All the curves exhibited work hardening (stress increase with the increase in strain) at a small strain, and flow softening (stress decrease with the increase in strain due to dynamic recrystallization) at a large strain. Further, a sharper flow softening was observed in the (Ti, Al)-added MEA compared with the (Ti, Al)-free MEA. In both samples, the flow stress increased with the increase in the strain rate. Constitutive equations were also constructed to describe the flow behaviors. The apparent activation energies were 401.08 kJ/mol (CoCrNi) and 566.13 kJ/mol ((CoCrNi)₉₆Ti₃Al₃), much higher than that of dilute alloys. This indicates the sluggish diffusion of elements in the MEAs.

The microstructure evolutions were carefully characterized. As displayed in Fig. 2, the fraction of recrystallization has a positive correlation with the temperature, and a negative correlation with the strain rate. A higher fraction of recrystallized grains was obtained at a higher temperature and low strain rate. The average size of recrystallized grains also has a positive correlation with temperature and a negative correlation with the strain rate, which demonstrates

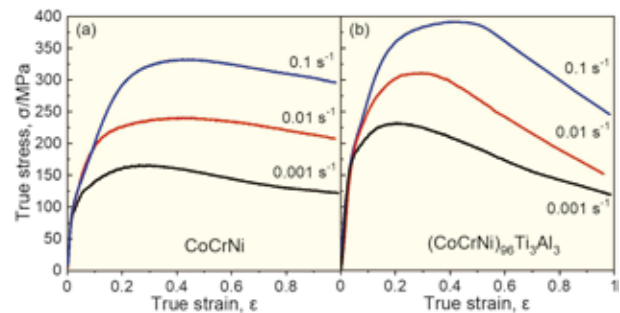


Fig. 1 Stress-strain curves of (a) CoCrNi and (b) (CoCrNi)₉₆Ti₃Al₃ MEA compressed at 1173 K with strain rate of 0.1, 0.01, and 0.001 s⁻¹.

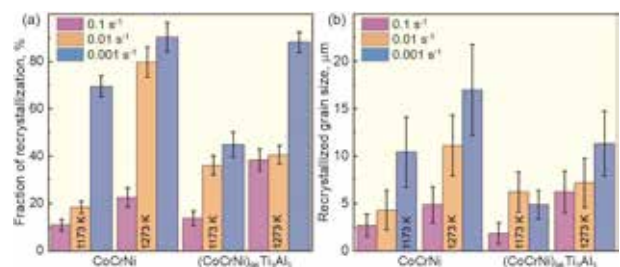


Fig. 2 The volume fraction (a) and average grain size (b) of the recrystallized grains in the CoCrNi and (CoCrNi)₉₆Ti₃Al₃ MEA hot-compressed to a true strain of 1.0 at 1173 K and 1273 K.

faster grain growth at higher temperatures. Fine grains were produced by continuous and discontinuous recrystallization mechanisms. The addition of Ti and Al impeded the grain growth at elevated temperatures. The present study sheds light on refining the microstructures of HEAs and MEAs.

References

- [1] Y. Zhao, T. Yang, Y. Tong, J. Wang, J.H. Luan, Z.B. Jiao, D. Chen, A. Hu, C.T. Liu, and J.J. Kai, *Acta Mater.* **138**, 72 (2017).
- [2] H. Yi, D. Wei, Y. Wang, L. Wang, M. Fang, K. Yang, and H. Kato, *Metals* **10**, 1341 (2020).

Keywords: deformation, microstructure, mechanical properties

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Variation in the Number of PhD Holders in Computational Materials Science: Importance of Higher Education of Computational Materials Science

Professional development Consortium for Computational Materials Scientists (PCoMS) supports young researchers in computational materials science (CMS) to develop a broader view and gain extensive knowledge of interdisciplinary areas in materials science, condensed matter physics, molecular science, and materials design. Here, we introduce a recent study by key members of PCoMS. Prof. Terada and coauthors analyzed the trend of human resource development in doctorate holders in CMS in Japan.

The recent progress in computational materials science (CMS), materials informatics, and related subjects has accelerated the discovery of advanced and novel materials. However, there have been only a few quantitative analyses regarding the change in the number of doctoral degree holders (doctors) in CMS in Japan.

We analyzed approximately 150 thousand doctoral dissertations from the engineering and science (ES) divisions of all national universities, major public universities, and private universities using text data mining techniques last 50 years. We sorted doctoral theses with titles containing keywords related to CMS and estimated the number of doctors in CMS.

In Japan, universities are classified into three categories: research universities (research Us), local education-oriented universities (education Us), and special education-oriented universities (special Us). The majority of doctors have been traditionally fostered in research Us. However, new doctoral courses in the education Us have been established since the 1990s due to the reconstruction of the graduate school. Thereafter, about 1/3 doctors are fostered in education Us. The number of doctors fostered in special Us in Japan is small even today.

From the analysis, we found that research Us are leading the national trend of the number of doctors in ES and CMS and the ratio of the number of doctors in CMS to those of doctors in ES in Japan. It increased rapidly in the beginning and then dropped rapidly. However, the rate of decrease in CMS thereafter is small. Therefore, the ratio of doctors in CMS to the doctors in ES continued to increase, closing to about 0.10 in 2018, as shown in Fig.1(a). On the other hand, change in the number of doctors in ES (especially in engineering) in education Us followed those of research Us and the national trend. However, the ratio of the number of doctors in CMS to those of doctors in ES at education Us was almost constant and small, approximately 0.05, as can be seen from Fig.1(b). As a reference, the ratio of the doctors in CMS to the doctors in ES in the California Institute of Technology (Caltech), which is one of a research Us in the USA, is almost constant and approximately 0.10–0.15.

We also investigated the appearance frequency of

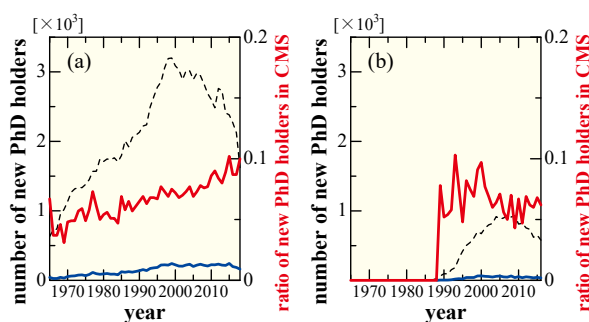


Fig.1 Number of new PhD holders in Japan. (a) research universities and (b) local education-oriented universities. --- : total number of new PhD holders in ES. — : number of new PhD holders in CMS. — : ratio of new PhD holders in CMS to PhD holders in ES.

keywords in the titles of theses. We found that keywords related to application appeared most frequently in theses from education Us. On the other hand, keywords related to theory appeared most frequently in theses from Caltech compared to those in research Us in Japan. This indicates that compared with education Us, research Us foster researchers who are more oriented toward fundamental research. It also indicates that Japanese universities foster researchers who are more inclined toward applied research and practical research compared to the universities in the USA.

Additionally, we found that the ratio of number of doctors in CMS in new majors, such as mathematical science, information science, and so on, is greater than that in traditional fields such as ES, though the traditional majors continue to be dominant in Japan.

These results indicate that the importance of research in CMS is increasing and that the number of doctors in CMS, who are oriented toward fundamental research in both research Us and education Us in Japan, should be increased [1].

References

- [1] Y. Terada and T. Mohri, "Recent changes in doctoral holders of computational materials science in Japan - recent diversity of specialties in diploma", JIM Annual Fall Meeting 2020, Sep 16, 2020.

Keywords: computational materials science, higher education

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Energy-Related Materials

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Effect of {111} Polarity on the Growth Rate During the Solidification of Compound Semiconductor GaSb

The twin formation and propagation during the directional solidification of GaSb was directly observed, and the effect of twinning on the growth rate of the GaSb{111} plane was clarified. The growth rate parallel to the $\langle 111 \rangle$ direction decreased after twinning, indicating that the polarity reversal by twinning significantly influenced on the growth kinetics of the {111} plane.

Large-sized single crystals of compound semiconductors are difficult to grow because defects, such as twin boundaries and dislocations, are significant during solidification. As the defect formation mechanism remains poorly understood, a universal technique for the single-crystal growth of compound semiconductors has yet to be established. The sphalerite structure in compound semiconductors, such as GaSb and GaAs, exhibits polarity in the $\langle 111 \rangle$ direction; therefore, the {111} $\Sigma 3$ twin boundary exhibits two possible atomic structures, and the difference between twin structures influences grain growth. However, the effect of the twin atomic structure on the growth dynamics of compound semiconductors is not completely understood. In this study, we directly observed twinning processes during the solidification of polycrystalline GaSb and clarified the effect of twinning on the grain growth rate [1].

The direct observation system consisted of a furnace and digital microscope. The furnace had two comb-shaped carbon heaters, between which a sample in a quartz crucible was placed and heated. The solidification of the sample was initiated by decreasing the currents applied to the heaters. The top surface of the sample was observed and recorded using a digital microscope. The moving distance of the crystal–melt interface was measured by tracing the position of the interface. The

orientations of grains in the areas observed were determined by electron backscatter diffraction method.

Figure 1 shows the effect of twinning on the competitive grain growth of GaSb. Three grains were present in the crystal (Fig. 1(a)). The boundary between Grains 1 and 2 was identified as a $\Sigma 3$ twin boundary, while that between Grains 2 and 3 was a random grain boundary. The shape of the crystal–melt interface remained the same before twinning. The twin nucleation was identified at the junction of the crystal–melt interface. The twin boundary between Grains 1 and 2, and the newly formed twin boundary propagated along the crystal–melt interface (Fig. 1(b)). The growth rate of Grain 2 along the direction parallel to $\langle 111 \rangle$ was reduced by half owing to the formation of the twin boundary, which resulted in the growth of Grain 2 being surpassed by adjacent grains (Fig. 1(c)). This indicates that polarity reversal occurred, and the growth direction turned to $\langle 111 \rangle_A$ owing to the formation of a reflection twin. Thus, the {111} polarity significantly affected the grain growth rate during the solidification of GaSb.

References

- [1] K. Shiga, K. Maeda, H. Morito and K. Fujiwara, *Acta Mater.* **185**, 453 (2020).

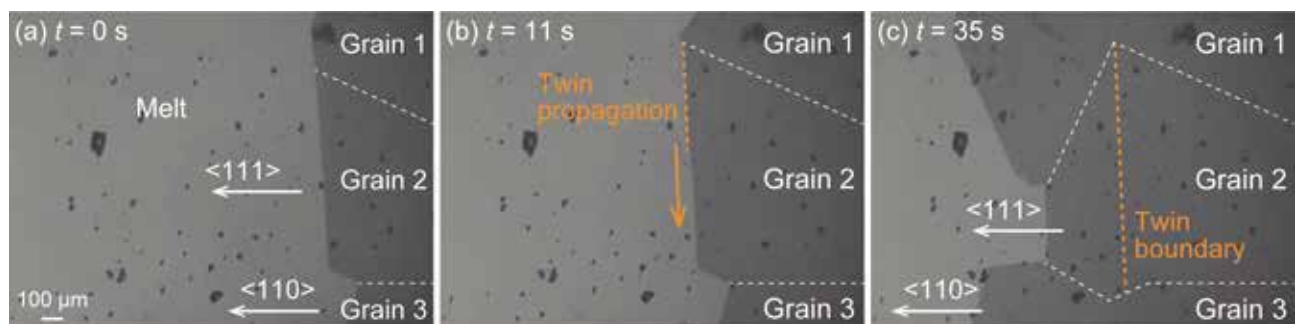


Fig.1 Photographic images of a moving crystal–melt interface during directional solidification of GaSb: (a) before twinning, (b) at twinning, and (c) after twinning.

Keywords: crystal growth, defects, kinetics

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Computational Simulations for Super-Low-Friction and High-Wear-Resistant Materials Design

The design of low-friction and high-wear-resistant materials requires a deep understanding of multiphysics phenomena, such as reaction, friction, impact, and stress. Therefore, we developed computational simulation methodologies for the theoretical design of super-low-friction and high-wear-resistant materials based on first-principles calculations and reactive molecular dynamics simulations.

Super-low friction and high-wear-resistant technologies are important not only for reducing energy loss but also for improving the durability of industrial machines. For example, carbon-based materials and silicon-based ceramics exhibit low friction properties. However, their friction and wear mechanisms are difficult to elucidate because these processes include multiphysics phenomena, such as chemical reaction, friction, impact, and stress. Therefore, we developed computational simulation methodologies for the theoretical design of super-low friction and high-wear-resistant materials based on first-principles calculations and reactive molecular dynamics (MD) simulations. These methods were applied to various friction systems and successfully 1) established theoretical wear law at the nanoscale [1]; 2) clarified the low-friction mechanism of Si-doped diamond-like carbon (DLC) [2]; and 3) proposed a super-low friction mechanism of silicon-based ceramic materials in water lubrication [3].

To prevent energy loss and device failures in micromachines, the theoretical design of anti-wear materials at the nanoscale is necessary. The conventional Archard's law can depict wear in macroscale contact, but it cannot describe nanoscale wear induced by chemical reactions. Thus, we proposed a non-empirical and robustly applicable wear law for nanoscale contact [1]. To confirm its robustness and applicability, we compared the amount of wear according to our proposed wear law with that by reactive MD simulations. Figure 1a shows the ball-on-disk friction model of DLC; its wear amounts are shown in Fig. 1b. Figure 1b indicates that our proposed wear law successfully reproduced the wear amounts obtained by reactive MD simulations, proving its robustness and applicability.

Experimentally, it is known that Si-doping of DLC film leads to super-low friction; however, its mechanism has not been clarified. Therefore, we investigated the structural changes in DLC by Si-doping via first-principles calculations [2]. Replacing Si atoms with C atoms on a diamond (111) surface caused large stress around the doped Si atom, and induced the transition of a six-membered C-ring into a five-membered C-ring.

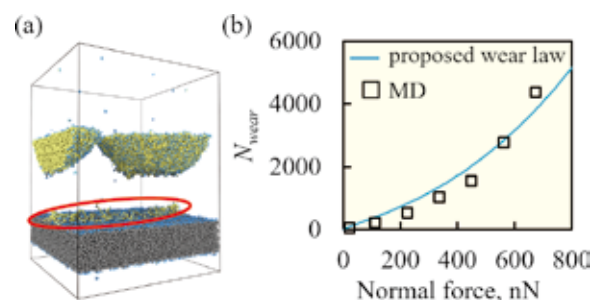


Fig. 1 (a) Snapshots of MD simulation in ball-on-disk contacts of DLC. The worn atoms are indicated by the red circles. (b) Wear amounts obtained by our proposed wear law and MD simulation.

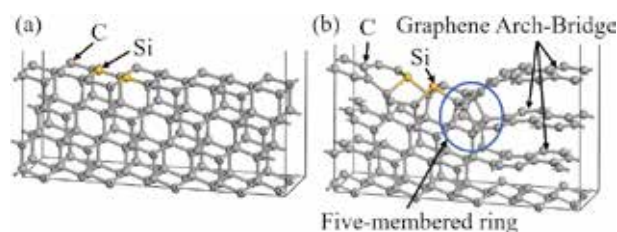


Fig. 2 (a) Initial and (b) optimized Si-doped diamond (111) structures, where two C atoms in the first layer are substituted with two Si atoms.

This led to the generation of the “graphene arch-bridge” (Fig. 2), which differs from a simple graphene structure because both of its ends are pinned to the diamond surface. This “graphene arch-bridge” structure affords the lower wear properties of Si-doped DLC compared with simple graphene because its ends are pinned to the DLC surface.

References

- [1] Y. Wang, J. Xu, Y. Ootani, N. Ozawa, K. Adachi, and M. Kubo, *Adv. Sci.* **8**, 2002827 (2021).
- [2] S. Bai, J. Xu, Y. Wang, Q. Zhang, T. Tsuruda, Y. Higuchi, N. Ozawa, J. M. Martin, K. Adachi, and M. Kubo, *J. Phys. Chem. C* **124**, 26379 (2020).
- [3] Y. Ootani, J. Xu, N. Takahashi, K. Akagami, S. Sakaki, Y. Wang, N. Ozawa, T. Hatano, K. Adachi, and M. Kubo, *J. Phys. Chem. C* **124**, 8295 (2020).

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In Situ Observation of Dislocation Loop Behavior During Annealing by WB-STEM in Neutron-Irradiated Reactor Pressure Vessel Steel

The dynamic behavior of loops and interactions between loops as well as loops and dislocations play key roles in microstructure variation, which is strongly connected to radiation-induced embrittlement in reactor pressure vessel (RPV) steels. The dedicated weak-beam scanning transmission electron microscope at the Oarai center was employed to observe and analyze the coalescence of loops and the interactions between loops and dislocations during annealing in neutron-irradiated RPV steel.

Neutron-irradiation-induced defects, especially dislocation loops, significantly contribute to embrittlement in reactor pressure vessel (RPV) steels during the long-term operation of nuclear power plants [1]. Therefore, understanding the thermal stability of defects is crucial.

The Burgers vector of dislocation loops is an important factor in microstructural evolution. In iron-based ferritic steels, the formation of $\langle 100 \rangle$ loops becomes more dominant than the formation of $\frac{1}{2} \langle 111 \rangle$ loops with the increase in irradiation temperature. However, the mechanism behind the transformation of $\frac{1}{2} \langle 111 \rangle$ loops to $\langle 100 \rangle$ loops remains unclear.

In the Oarai center, weak-beam scanning transmission electron microscopy (WB-STEM) was developed to achieve a more accurate quantification of irradiation-induced defects [2]. In situ WB-STEM observation was performed during annealing for a surveillance test specimen of RPV steel, which was neutron-irradiated to a fluence of 8.2×10^{23} neutrons·m⁻².

As shown in Fig. 1(a) and (b), this is the first time to directly observe that two $\frac{1}{2} \langle 111 \rangle$ dislocation loops collided with each other and coalesced to form a $\langle 100 \rangle$ dislocation loop. Small $\frac{1}{2} \langle 111 \rangle$ dislocation loops could be absorbed by large $\langle 100 \rangle$ dislocation loops, whereas the Burgers vector of the $\langle 100 \rangle$ loops remained unchanged, as illustrated in Fig. 1(c) and (d). Dislocation decoration by loops occurred during annealing because of the interaction between the dislocations and loops. The dislocations decorated by loops forming helical configurations were fairly stable during the continuous annealing process [3].

This study provides direct experimental evidence for the formation mechanism of $\langle 100 \rangle$ dislocation loops and provides a better understanding of the temperature-dependence of dislocation loop evolution.

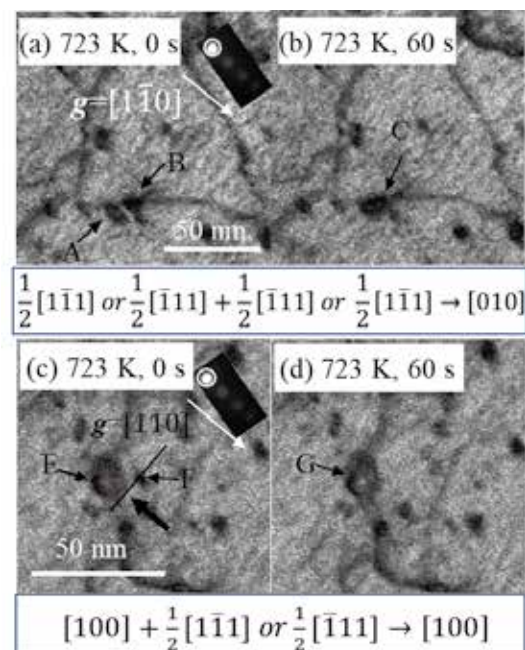


Fig. 1 In situ observation of dislocation loop evolution in neutron-irradiated RPV steel during annealing at 723 K with diffraction vector $g = [1\bar{1}0]$ near $[001]$ zone axis in STEM mode: (a) (b) loop coalescence; (c) (d) loop absorption.

The interaction between loops and dislocations suggests a new mechanism of loop-impeding dislocation motion.

References

- [1] M. Shimodaira, T. Toyama, K. Yoshida, K. Inoue, N. Ebisawa, K. Tomura, T. Yoshiie, M. J. Konstantinovic, R. Gerard, and Y. Nagai, *Acta Mater.* **155**, 402 (2018).
- [2] K. Yoshida, M. Shimodaira, T. Toyama, Y. Shimizu, K. Inoue, T. Yoshiie, M. J. Konstantinovic, R. Gerard, and Y. Nagai, *Microsc.* **66**, 120 (2017).
- [3] Y. Du, K. Yoshida, Y. Shimada, T. Toyama, K. Inoue, K. Arakawa, T. Suzudo, M. J. Konstantinovic, R. Gerard, Somei Ohnuki, and Y. Nagai, *Materialia*. **12**, 100778 (2020).

Keywords: microstructure, nuclear materials, defects

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Role of Crystal Lattice Defects in Polycrystalline SiC Corrosion

Irradiation-accelerated corrosion is a problem when SiC is exposed to extreme environments, such as particle beams. The relationship between lattice defects and corrosion was investigated using electrochemistry and electron spin resonance. The corrosion rates increased with dangling bond (DB) density, indicating that DBs were the primary reaction sites. Further, the lattice distortion associated with dense DBs was found to be the primary source of corrosion acceleration.

Materials resistant to extreme conditions, such as oxide dispersion-strengthened alloys [1], ceramics [2], and semiconductors [3], are crucial to realize advanced nuclear systems. Silicon carbide (SiC) exhibits outstanding irradiation stability and strength at high temperatures, which has led its numerous applications along with its composites in structural and core components of fusion reactors, and nuclear fuels. These environments are highly corrosive and involve exposure to hot water and high-temperature steam. Our previous study first reported that the corrosion rate increased when various lattice defects were created by ion irradiation. Then, researchers subsequently reported the irradiation-accelerated corrosion of SiC in various coolants.

Longer irradiation times lead to the accumulation of lattice damage, thereby accelerating corrosion. However, the reason for this acceleration remains unknown, and there are no clear guidelines for corrosion protection. We hypothesized that unpaired electrons (or dangling bonds, DBs) that formed at the vacancies contributed to the reaction.

The relationship between lattice defects and the corrosion of SiC irradiated with heavy ions was investigated using electrochemistry and electron

spin resonance (ESR) spectroscopy. An immersion test in high-pressure hot water was also used to evaluate surface recession.

Surface recession, corrosion current, and DB density increased after irradiation. The changes were more pronounced at lower irradiation temperature. The corrosion current increased monotonically with DB density, indicating that DBs were the primary reaction site. Further, the surface recession rate in hot water increased exponentially with increasing DB density. The largest number of DBs were induced during irradiation at the lowest temperature. These DBs were surrounded by a distorted lattice because of the absence of lattice recovery during irradiation. These findings [2] indicate that corrosion was accelerated by the accumulation of excess DBs and the surrounding lattice distortion.

References

- [1] H. Wang, H. Yu, S. Kondo, N. Okubo, and R. Kasada, *Corros. Sci.* **175**, 108864 (2020).
- [2] S. Kondo, K. Seki, Y. Maeda, H. Yu, K. Fukami, and R. Kasada, *Scr. Mater.* **188**, 6-9 (2020).
- [3] Y. Okuno, N. Ishikawa, M. Akiyoshi, H. Ando, M. Harumoto, and M. Imaizumi, *J. App. Phys.* **59**, 074001 (2020).

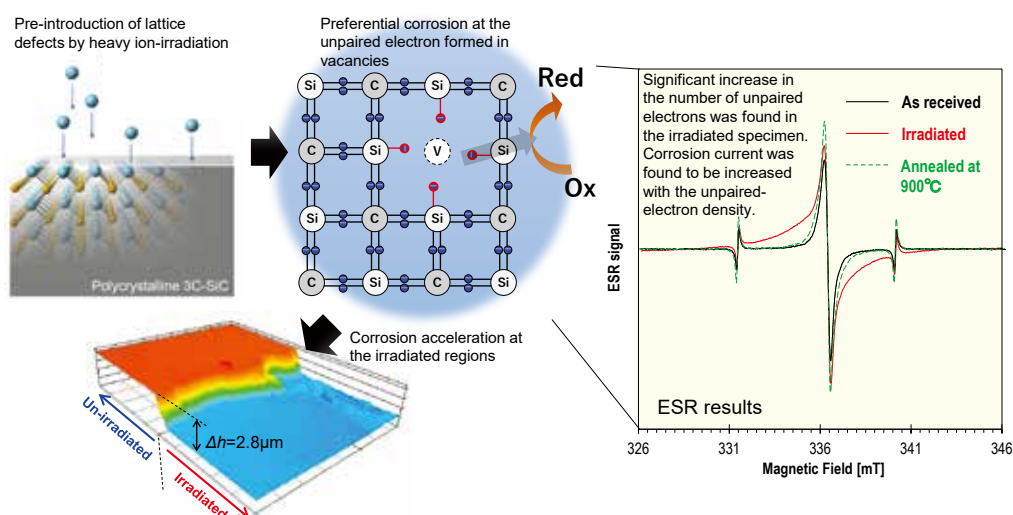


Fig.1 A schematic view of SiC with irradiation-induced defects and corrosion starting from the defects (left). ESR results show an increase in DB with irradiation and a decrease with defect recovery (right).

Keywords: ceramic, corrosion, defects

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Novel Hierarchical Nanoporous Graphene Nanoplatelets with Excellent Rate Capabilities Produced via Self-Templating Liquid Metal Dealloying

Hierarchical nanoporous graphene nanoplatelets (HNGNPs) with high crystallinity and a moderate specific surface area are synthesized by liquid metal dealloying. The large surface area, high crystallinity, and structural robustness of the mutually interconnected hierarchies of the HNGNPs result in their excellent rate capabilities and cycling stability in lithium-ion batteries.

Significant efforts have been made to develop carbon nanomaterials that meet the demands of high capacity, long cycle performance without degradation, and high-rate charge/discharge performance to realize advanced lithium-ion batteries (LIBs). In particular, the good electric conductivity and short diffusion path of lithium ions are necessary to enhance the rate capability. A hierarchical open porous structure has been proposed to facilitate efficient electrolyte access and accelerate electron percolation to obtain superior performance, especially the high-rate capability required for LIBs. Such hierarchical structures are prepared using specific templates, but the shapes of templating materials are generally restricted.

In this work, we designed a liquid metal dealloying (LMD) process to develop hierarchical nanoporous graphene nanoplatelets (HNGNPs) as anode active materials of LIBs to achieve high rate capability [1]. Based on the miscibility among the elements, a $\text{Mn}_{78}\text{C}_{22}(\text{at}\%)$ precursor and a Bi melt were selected for the LMD reaction, in which the selective dissolution of Mn in Bi melt and formation of porous carbon occurred.

Figure 1(a) shows the microstructure of the product dealloyed in the Bi melt at 1200 °C for 3 min. The mesoporous network of GNPs formed the lower hierarchy, which was nested within the much larger network (macropores) of the upper hierarchy. This LMD process enabled the synthesis of well-defined hierarchical nanoarchitectures on two different length scales without any additives. Such hierarchical morphology results from the self-template effect due to the unique phase transformation during the LMD reaction. During the Mn depletion, the precursor transformed into the intermetallic Mn_7C_3 compound with the development of the upper hierarchy of the micron-sized large ligament. With the further depletion of Mn, this intermetallic compound transformed into graphite with the development of the lower hierarchy of the nanometer-sized pores within the ligaments.

The optimized microstructural characteristics of the HNGNPs include high crystallinity (interlayer distance of the (002) plane of ~ 0.341 nm and intensity ratio of the Raman G- and D-bands of ~ 0.552); a moderate specific surface area (~ 152.7 m² g⁻¹); and a bimodal pore size distribution with the highest peak at 126 nm and an additional peak at 457 nm.

The rate capability of the HNGNPs was evaluated at various rates from 0.2C to 20C (1C = 0.372 A/g) and compared

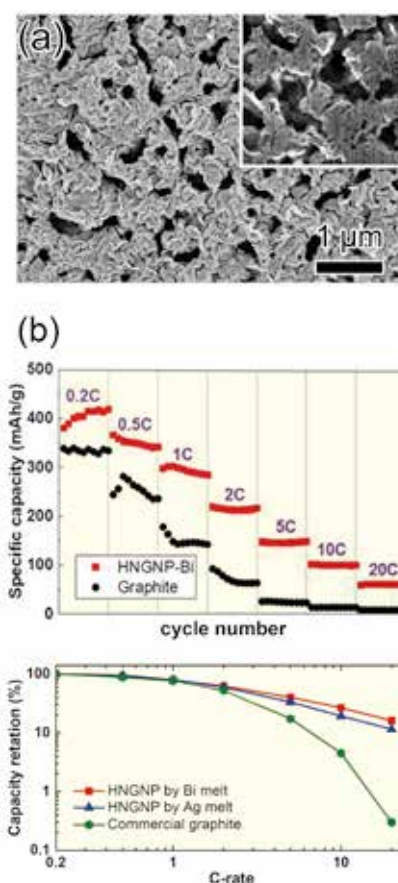


Fig.1 (a) Microstructure and (b) rate capability of HNGNP anode prepared by LMD process [1]. The inset in (a) shows cross sectional structure of the ligaments.

with a commercial artificial graphite sample. As shown in Fig.1(b), the HNGNP electrodes exhibited superior capacity retention to the commercial artificial graphite, especially at a high C-rate, demonstrating the beneficial role of their hierarchical nanoporous structure developed via LMD. These favorable features of the HNGNP electrode can be attributed to its mutually interconnected hierarchical structure with large surface area, moderate crystallinity, and high stability.

References

- [1] W.-Y. Park, T. Wada, S.-H. Joo, J. Han, and H. Kato, *Mater. Today Commun.* **24**, 101120 (2020).

Keywords: dealloying, porosity, energy storage

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Pseudorotating Hydride Complexes with High Hydrogen Coordination: A New Class of Rotatable Polyanions in Solid Matter

Solid-state materials containing rotatable polyanions constitute a peculiar class of ionic conductors owing to their unique transport behavior, i.e., rotating polyanions promote phase transitions to disordered phases with cation conductivities enhanced by several orders of magnitude. A major drawback is the high temperature required to activate rotation and the corresponding low conductivities at room temperature. Here, we propose a mechanism to drastically reduce the temperature based on the use of pseudorotation in high-H coordination hydride complexes. We demonstrate this mechanism for an existing hydride $\text{Li}_5\text{MoH}_{11}$ containing MoH_9^{3-} and demonstrate that this material can exhibit an unprecedentedly high lithium-ion conductivity at room temperature.

There is currently a strong demand to replace organic liquid electrolytes used in conventional rechargeable batteries with solid-state electrolytes owing to their advantages, such as improved safety and higher energy density. Much effort has been devoted to identifying materials with superior transport properties.

Among the diverse solid-state electrolytes, those containing polyanions, such as $\text{B}_{12}\text{H}_{12}^{2-}$ (Fig. 1 (a)), constitute a peculiar class of materials because of their unique transport behavior, i.e., polyanions rotate at an elevated temperature, thereby promoting phase transitions with cation conductivities enhanced by several orders of magnitude. However, a major drawback is the high temperature required to activate rotation and the corresponding low conductivities at room temperature (RT).

In this study, we adopt a novel approach to reduce the transition temperature based on the use of homoleptic transition metal hydride complexes, wherein hydrogen is the sole ligand species, covalently binding to single transition metals (Fig. 1 (b)). The rationale behind this choice is that, unlike other polyanions, the rotation only requires small displacements of highly mobile hydrogen, which could therefore be expected to occur with low activation energy.

We found that MoH_9^{3-} in $\text{Li}_5\text{MoH}_{11}$ exhibits pseudorotation with a remarkably low activation energy of ~ 20 meV. This motion yields a large entropic contribution of $19.1 \text{ J/mol} \cdot \text{K}$, which stabilizes the lithium-ion conducting phase even below RT. The RT lithium-ion conductivity reached $7.9 \times 10^{-2} \text{ S cm}^{-1}$ [1], which is more than three times greater than the highest value of $2.5 \times 10^{-2} \text{ S cm}^{-1}$ previously reported for a sulfide $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ [2] (Fig. 2).

The mechanism is quite general in principle and would be useful in lowering the temperature to activate the rotation of polyanions. This is expected

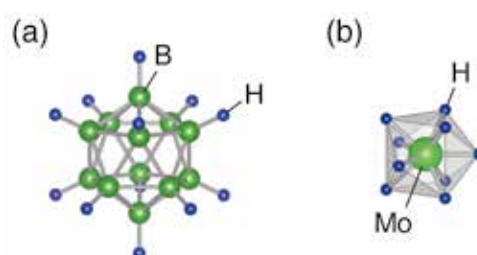


Fig. 1 Typical polyanions found in solids: (a) $\text{B}_{12}\text{H}_{12}^{2-}$, and (b) MoH_9^{3-} .

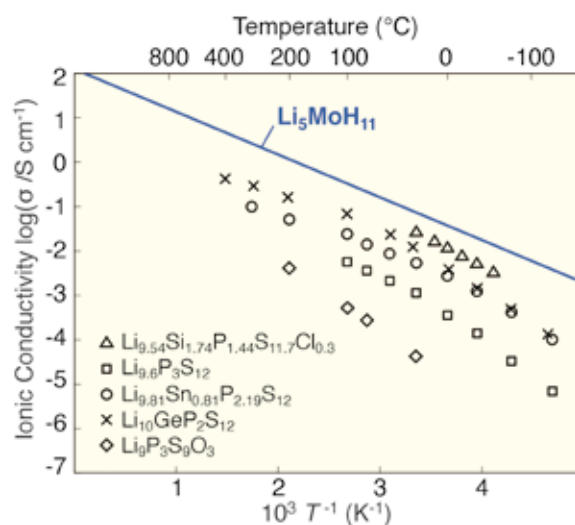


Fig. 2 Arrhenius plot of lithium-ion conductivity of $\text{Li}_5\text{MoH}_{11}$. Data for typical sulfides are shown for comparison.

to help identify compositions that are amenable to RT superionic conductors.

References

- [1] S. Takagi, T. Ikeshoji, T. Sato, and S. Orimo, Appl. Phys. Lett. **116**, 173901 (2020).
- [2] Z. Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, and R. Kanno, Nature Energy **1**, 16030 (2016).

Keywords: solid-state electrolytes, hydride, first principles calculations

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Quantitative Analysis of Hydrogen in High-Hydrogen-Content Materials via Laser-Induced Breakdown Spectroscopy

An analytical approach that can rapidly determine the hydrogen concentrations in solid-state materials is needed to contribute to the hydrogen economy. We established a method that can estimate hydrogen concentrations ranging from 0.2 to 7.6 mass% within a few seconds via laser-induced breakdown spectroscopy.

The demand for the quantitative analysis of hydrogen in solid-state substances has recently grown owing to the increasing studies on materials related to hydrogen production, transportation, storage, and utilization. Several analytical techniques are currently being used for this purpose, but their application areas are limited. Moreover, they are not rapid analytical methods. This study developed laser-induced breakdown spectroscopy (LIBS), which can rapidly quantify hydrogen concentrations in solid-state substances within a few seconds. Magnesium hydride (MgH_2) was selected as the target sample.

A straight-line calibration curve was obtained by measuring the hydrogen emission intensity (at 656.28 nm) for standard Mg/MgH_2 mixtures containing 0, 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 7.6 mass% of hydrogen in a 3000 Pa helium atmosphere (Fig. 1) [1]. In the LIBS measurement, the residual water molecules in the samples and the LIBS gas line were removed using a desiccator containing silica gel and using a moisture trap, respectively. The lower limit of quantification was estimated to be 0.20 mass% from the calibration curve, indicating a determinable hydrogen concentration range of 0.2–7.6 mass%. We also found that reducing the residual water molecules in the gas line (including the gas cylinder), by heating the gas line and/or attaching more moisture traps, is important to quantify ppm concentrations with the LIBS system.

By using the calibration curve (Fig. 1), we estimated the hydrogen concentrations of MgH_2 samples heated at 350 °C for 2, 4, and 6 h in an argon atmosphere. The results were consistent with those obtained through inert gas fusion/gas chromatography, which is the conventional method for measuring the hydrogen content of solid-state substances (Table 1) [1]. Our results demonstrate the feasibility of the rapid quantitative analysis of hydrogen in MgH_2 via LIBS. The LIBS technique is also applicable to two- and three-dimensional analyses.

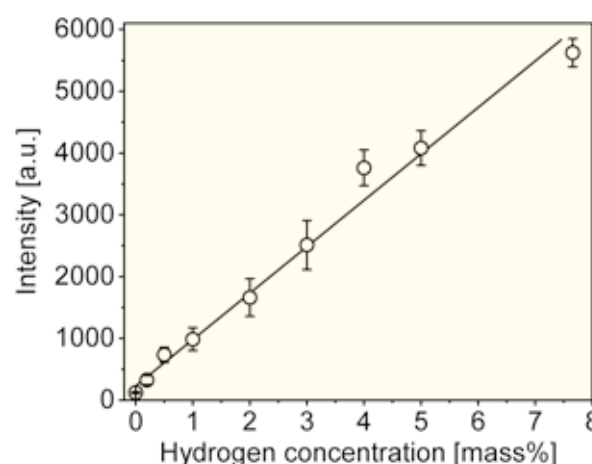


Fig. 1 Calibration curve based on the intensity of the hydrogen emission line (H I 656.28 nm) measured in reduced helium (3000 Pa) atmosphere.

Heating time [h]	LIBS		Inert gas fusion/gas chromatography
	Intensity [a.u.]	Hydrogen concentration [mass%]	Hydrogen concentration [mass%]
2	5727 ± 130	7.3 ± 0.2	7.62 ± 0.05
4	1786 ± 261	2.0 ± 0.4	2.62 ± 0.11
6	366 ± 121	0.1 ± 0.2	0.43 ± 0.02

Table 1 Intensity of hydrogen emission Line (H I 656.28 nm) via LIBS spectra from MgH_2 samples heated at 350 °C for different times under argon flow, and the derived hydrogen concentration, along with the hydrogen content estimated via inert gas fusion/gas chromatography.

References

- [1] S. Imashuku, T. Kamimura, S. Kashiwakura, and K. Wagatsuma, *Anal. Chem.* **92**, 11171 (2020).

Keywords: atomic emission spectrometry, hydrogen

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Development of High-Performance Spinel-Oxide Cathode Materials for Magnesium Rechargeable Batteries

Magnesium rechargeable batteries (MRBs) are a promising candidate for next-generation batteries. However, their development has been hindered by the lack of cathode materials. We proposed a new design concept and demonstrated that defect spinel ZnMnO_3 has significantly high cyclability among the high-potential (2–3 V class) spinel-oxide materials for MRBs.

To realize a future sustainable society, it is essential to develop next-generation batteries combining high safety and energy density. Magnesium rechargeable batteries (MRBs) have attracted much attention because Mg can be deposited without dangerous dendritic growth, enabling its use as a high-capacity anode material. However, establishing oxide cathode materials that allow reversible Mg insertion/extraction is a challenge because these readily transform into irreversible MgO -like rock salt phases by Mg insertion. Although we have been developing spinel-oxide cathode materials for MRBs, they exhibit rapid capacity fading, possibly due to the spinel-to-rock-salt transition.

In this study [1], we propose the concept of utilizing "defect" spinel oxides to prevent the irreversible transformation by Mg insertion. Defect spinel oxides contain cation deficiencies at octahedral sites in the spinel structure. The cation-deficient sites are expected to provide migration pathways and accommodation sites for Mg^{2+} ions, as illustrated in Fig. 1a. Defect spinel oxides, denoted as ABO_3 , generally consist of divalent $A(\text{II})$ and tetravalent $B(\text{IV})$ cations. We chose Zn and Mn as the A and B cations, respectively, because Zn stabilizes the spinel phase due to the strong preference for the tetrahedral sites, while Mn is stable at a relatively high valence state.

Nanocrystalline ZnMnO_3 was synthesized for use

in preparing the electrodes. Detailed electrochemical measurements and structural analysis of the electrodes after discharge/charge revealed that Mg^{2+} ions were preferentially inserted into the cation-deficient sites that maintain the spinel-based structures. This is in strong contrast with the stoichiometric spinel oxide materials for MRBs, e.g., MgCo_2O_4 , which readily undergo the spinel-to-rock-salt transition.

To investigate the cyclability of defect spinel ZnMnO_3 , a battery cycling test was carried out at 150 °C to facilitate Mg^{2+} diffusion in the cathode material. As shown in Fig. 1b, the discharge capacity of ZnMnO_3 was ~100 mAh/g even after 100 cycles with a high coulombic efficiency. Such long-term cyclability has never been achieved using stoichiometric spinel oxides. By assuming the ideal redox potential of the Mg-metal anode, the energy density of Mg/ZnMnO_3 cell was estimated to be 200–300 Wh/kg, which is comparable to that of conventional Li-ion batteries. Because of the advantages in terms of safety and element resources, this battery system is promising for large-scale applications, such as electric vehicles and stationary energy storage systems.

References

- [1] K. Shimokawa, T. Atsumi, N. L. Okamoto, T. Kawaguchi, S. Imashuku, K. Wagatsuma, M. Nakayama, K. Kanamura, and T. Ichitsubo, *Adv. Mater.* **33**, 2007539 (2021).

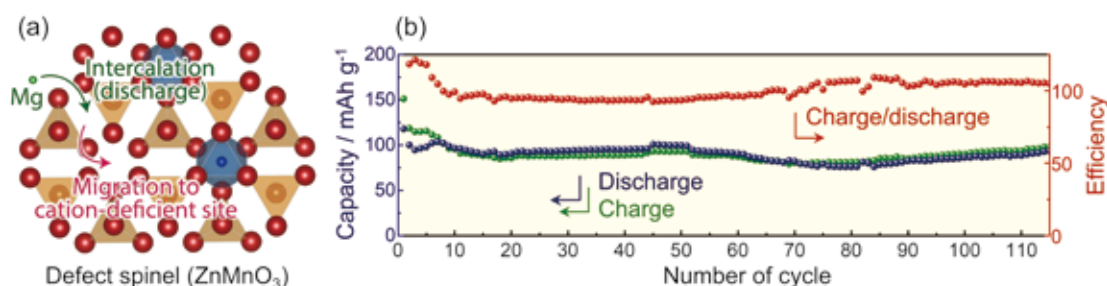


Fig. 1 (a) Schematic illustration showing the expected migration pathway of Mg^{2+} ions in defect spinel ZnMnO_3 . In contrast to stoichiometric spinel oxides, Mg^{2+} ions can be stored in the cation-deficient sites that suppress the spinel-to-rock-salt transition. (b) Long-term cyclability of the defect spinel ZnMnO_3 in the electrolyte of (Mg10/Cs90)-TFSA at 150 °C.

Keywords: energy storage, defects, oxide

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Electronic Materials

IMR KINKEN Research Highlights 2021



Hopfield Neural Network with Intrinsic Learning in Magnetic Films

Macroscopic spin ensembles possess brain-like features, which offer opportunities for neuromorphic computing by spintronics devices. We propose a four-node Hopfield network based on magnetic textures. Its synapses do not require external input to update weights as this occurs intrinsically via physical feedback mechanisms built into the texture.

Over the last decade, tremendous progress has propelled neuromorphic computing to the forefront of information technology. However, brain-inspired algorithms are mainly emulated by conventional von Neumann architectures with physically separated computing and storage units, thereby limiting the power of artificial intelligence algorithms.

Spintronics is a leading candidate for hardware-implemented neuromorphic computing, in which analogue devices emulate neurons and synapse functions. However, practical implementations require the improved efficiency of the training and inference processes. To the best of our knowledge, the main problem of existing approaches is the need for external algorithms running on conventional computers to update the weights of the synapses during training.

We propose a neuromorphic computing platform with superior performance based on the plasticity of magnetic textures [1]. The physical requirements are a magnetic film with chiral domain patterns generated by the Dzyaloshinskii–Moriya interaction, anisotropic magnetoresistance, and current-induced spin-transfer torque [1]. We simulated the device performance by finite element simulations, which have been successfully applied to problems in spin cavitronics [2].

We show that an electrically conducting magnetic film can operate as a collection of artificial synapses with weights encoded by the conductance between external electrodes in a matrix configuration. A voltage applied to the magnetic thin film (Fig. 1(a)) drives the magnetic textures by the spin-transfer torque. With changes in the magnetic configuration, the conductance (or resistance) is modified by the anisotropic magnetoresistance. Figure 1(b) shows the enhanced horizontal conductance over time under a current, as the vertical conductance decreases. This “plasticity” encodes “weights” into magnetic textures.

We implemented this concept as a four-node Hopfield network in Fig. 1(c). The value of four neurons were encoded as voltage applied to four electrodes. The weight matrix was encoded into the

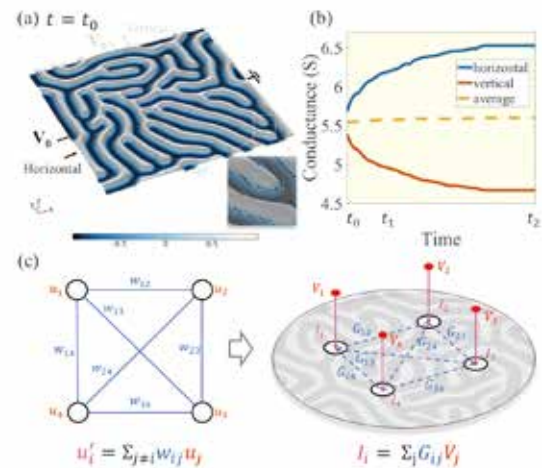


Fig. 1 (a) Configuration of magnetic texture at an initial time. Black (white) color represents up (down) magnetization perpendicular to the film and the arrows (inset) represent in-plane magnetization. (b) Conductance change in either the horizontal or vertical direction in the presence of an electric current. (c) Schematic four-node Hopfield network.

effective conductance matrix inside the magnetic film. The four-node Hopfield network can operate as an associative memory to memorize and recall a four-pixel binary picture. In the training stage, only the pattern to be memorized was applied in terms of binary voltages, and the network naturally updated the weights without requiring external computations. In the inferring stage, the network is fixed, and the stored patterns can be recalled by standard methods.

The learning rule is based on physical laws rather than human interference. The concept can be generalized to other materials with current-induced plasticity. Our work paves the way for hardware-based neuromorphic computing devices with on-chip learning.

References

- [1] W. Yu, J. Xiao, and G.E.W. Bauer, arXiv: 2101.03016 (2021).
- [2] W. Yu, T. Yu, and G.E.W. Bauer, Phys. Rev. B **102**, 064416 (2020).

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High Magnetic Field Element Specific Magnetization to Resolve the Magnetization Process of a Hard-Intermetallic Ferrimagnet

Nonmonotonic magnetic-field-dependence of magnetic moments in TmFe_5Al_7 were determined using high magnetic field X-ray circular magnetic dichroism. The complex behavior was caused by the competition between two different magnetic anisotropies and exchange coupling.

Rare-earth transition metal intermetallic compounds have been studied intensively for their strong anisotropies and large magnetic couplings. These are an important class of materials for hard magnets used in a wide range of applications, such as energy conversion and transport. High magnetic fields have been used to investigate the anisotropies and exchange couplings of these magnets, and important material parameters have been evaluated.

TmFe_5Al_7 has a ThMn_{12} -type structure with tetragonal symmetry. The alignment of the magnetic moments of Fe and Tm is determined by the balance between the easy-plane type anisotropy of Fe, the easy-axis type anisotropy of Tm, and the exchange coupling between Fe and Tm. It should be noted that the easy-axis type ferrimagnet ground state at low temperature is rare in the RFe_5Al_7 family, when R (rare earth element) is heavy rare-earth.

A magnetization curve in high magnetic fields was measured to examine the magnetic parameters of the system at the Dresden High Magnetic Field Laboratory. The bulk magnetization showed an upturn curvature up to 12 T, where a small jump in magnetization was observed. The curvature then became negative above 12 T. This indicates that there is a flop of magnetic moments at approximately 12 T. Despite the characteristic features found in the magnetization curve, the magnetic parameters or the alignment of magnetic moments could not be inferred.

The key to understanding the magnetization process is element-specific magnetization measurement with X-ray circular magnetic dichroism (XMCD) in a pulsed high magnetic field, which was developed by the collaboration between the magnetism division of the Institute for Materials Research, Tohoku University, and BL25 at SPring-8 [1]. In XMCD, the magnetic moment of a specific magnetic ion is deduced by tuning the X-ray energy to the related absorption edge. When soft X-rays are employed, the final states of the edge absorptions are the 3d orbitals of the transition element and the 4f orbital of the rare earth element, respectively. This is the advantage of using soft X-rays in XMCD despite the difficulty of using ultra-high vacuum. In BL25 at SPring8, the XMCD can be measured up to 40 T using a compact bipolar pulsed field generator.

Figure 1 presents the results of the element-specific

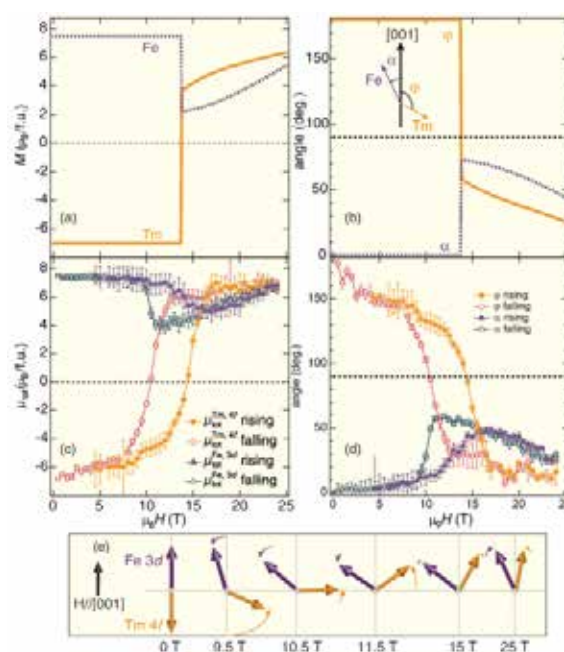


Fig. 1 Element-specific magnetization of Tm and Fe and the alignment of magnetic moment determined by XMCD [2].

magnetization curve and the change in the magnetic moment alignment in the magnetization process. It shows that Fe moments always align along the magnetic field with field-dependent tilting, while the Tm moment changes from collinear to spin-flopped-like arrangements around the transition found by the small bulk magnetization jump. This result can be understood as the balance between the magnetic anisotropies and exchange coupling. Such complex nonmonotonic magnetic-field-dependence of the Fe moment can be evaluated only by the XMCD technique in high magnetic fields. This method contributes to the study of various intermetallic magnetic compounds.

References

- [1] H. Yasumura, Y. Narumi, T. Nakamura, Y. Kotani, A. Yasui, E. Kishaba, A. Mitsuda, H. Wada, K. Kindo, and H. Nojiri, *J. Phys. Soc. Jpn.* **86**, 054706 (2017).
- [2] S. Yamamoto, D. I. Gorbunov, H. Akai, H., Yasumura, Y. Kotani, T. Nakamura, T. Kato, N. V. Mushnikov, A. V. Adreev, and H. Nojiri, *Phys. Rev. B* **101**, 174430 (2020).

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Conductive Oxide with Surface Polarity for Device Applications

A layered delafossite, PdCoO₂, is one of the most conductive oxides with a bulk conductivity comparable with those of Au metals. Charged layers of Pd⁺ and [CoO₂]⁻ alternate in the PdCoO₂ crystal structure, generating surface polarities that strongly influence the surface/interface properties. Using pulsed laser deposition, we successfully grew high-quality thin films of PdCoO₂ and fabricated functional devices: a nanodevice showing quantum transport and a diode that can operate at elevated temperatures. The superior properties of these devices are attributed to the anisotropic electrical conductivity of PdCoO₂ that originates from its unique layered crystal structure.

The layered oxide PdCoO₂ has attracted significant attention as a highly conductive metal comparable to the noble metals (Fig. 1). Using PdCoO₂ thin films [1], we are currently exploring novel electronic functionalities that originate from two key features of PdCoO₂: the high electron mobility (~51000 cm²/Vs for bulk single crystals) and surface polarity induced by the ionic layered structure (inset of Fig. 1). By fabricating submicron-scale Hall-bar devices using electron beam lithography, we carried out the first observation of quantum transport in PdCoO₂ thin films [2]. We found that the surface polarity of PdCoO₂ significantly affects the surface electronic states, giving the inherently nonmagnetic PdCoO₂ unique magnetic states in the vicinity of the Pd-terminated surfaces [3]. The interplay between surface magnetic states and quantum effects would be an interesting subject for future study.

The surface polarity of PdCoO₂ can improve the performance of practical and useful devices. We fabricated a crystalline heterointerface of PdCoO₂ and a wide-bandgap semiconductor β -Ga₂O₃. We found that the PdCoO₂/ β -Ga₂O₃ interface can function as a Schottky diode that performs current rectification even at a high temperature of 350 °C [4]. The PdCoO₂/ β -Ga₂O₃ diode can operate in the MHz frequency, which shows promise for high-frequency power electronic devices [5]. The PdCoO₂ exhibits superior Schottky properties by forming a bilayer with an elemental metal (tandem electrode). The junction between the tandem electrode and β -Ga₂O₃ has a wide range of Schottky barrier heights that can be fine-tuned by changing the thickness of PdCoO₂ [6]. The interface dipole effect was also found in the junction between β -Ga₂O₃ and PdCrO₂, a sister compound of PdCoO₂ [7], suggesting the universal role of surface polarity in these polar oxides.

These results demonstrate that PdCoO₂ and related metallic delafossites are a fascinating class

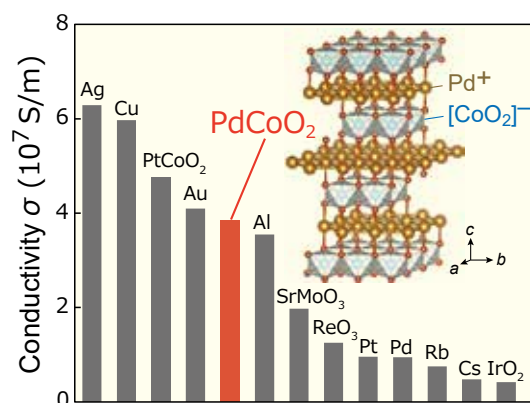


Fig. 1 Electrical conductivity of PdCoO₂ and various metals at room temperature. Inset: the crystal structure of PdCoO₂. The ionic layers of Pd⁺ and [CoO₂]⁻ are indicated.

of materials for basic physics and various applications. We will continue to explore exotic phenomena and functions in the heterostructures of metallic delafossites, which have high-mobility electrons and surface polarity in their simple (and beautiful) alternating layered crystal structures.

References

- [1] T. Harada, K. Fujiwara, and A. Tsukazaki, *APL Mater.* **6**, 046107 (2018).
- [2] T. Harada, P. Bredol, H. Inoue, S. Ito, J. Mannhart, and A. Tsukazaki, *Phys. Rev. B* **103**, 045123 (2021).
- [3] T. Harada, K. Sugawara, K. Fujiwara, M. Kitamura, S. Ito, T. Nojima, K. Horiba, H. Kumigashira, T. Takahashi, T. Sato, and A. Tsukazaki, *Phys. Rev. Res.* **2**, 013282 (2020).
- [4] T. Harada, S. Ito, and A. Tsukazaki, *Sci. Adv.* **5**, eaax5733 (2019).
- [5] T. Harada and A. Tsukazaki, *Appl. Phys. Lett.* **116**, 232104 (2020).
- [6] T. Harada and A. Tsukazaki, *APL Mater.* **8**, 041109 (2020).
- [7] T. Miyakawa, T. Harada, S. Ito, and A. Tsukazaki, *J. Appl. Phys.* **128**, 025302 (2020).

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Nanoscale Polarized π -Electron Clusters Probed by Noise Spectroscopy

We investigated the low-frequency charge-carrier dynamics of a molecular dimer-Mott insulator β' -(BEDT-TTF) $_2$ Cl $_2$, in which the freezing of charge fluctuations on the dimers gave rise to electronic ferroelectricity. Conductance noise spectroscopy proved the formation of a polar nanoscale region leading to glassy and relaxor-type ferroelectric behavior. Thus, conductance noise spectroscopy is a suitable tool for investigating electric-polarization dynamics in molecular and other charge-driven ferroelectrics.

The molecular organic dimer-Mott insulator β' -(BEDT-TTF) $_2$ Cl $_2$ is a model system for studying the underlying charge fluctuations on the dimers, where electric-field-induced charge disproportionation has been demonstrated in dielectric and pyroelectric properties [1] and Raman scattering [2]. β' -(BEDT-TTF) $_2$ Cl $_2$ exhibits relaxor-type ferroelectric behavior with a strong frequency-dependent peak of the dielectric constant developing below $T \sim 125$ K. At approximately below 60 K, pyrocurrent measurements reveal the onset of electric-field-induced macroscopic polarization. The P - E curves that show small values of the fully polarized moment and relaxation effects in Raman spectroscopy suggest a dipole-glass state at low temperatures.

We employed conduction current noise spectroscopy to study the dynamical charge fluctuations on strongly-correlated charge carriers in β' -(BEDT-TTF) $_2$ Cl $_2$ at low frequencies, i.e., in the mHz to kHz regime [3]. The method is complementary to dielectric spectroscopy and allows the extraction of spectroscopic information from electronic transport measurements. Our aim is to establish a connection between the fluctuating conductivity in the Mott insulating phases and relaxor ferroelectric properties.

Figure 1 demonstrates the normalized current noise power spectral density S_I at 130 K. In the temperature region of $110 \text{ K} < T < 140 \text{ K}$, a single Lorentzian spectrum, which is characteristic for a fluctuating two-level system, was found to be superimposed on the “background” $1/f$ noise spectrum. At temperatures higher and lower than this temperature region, we observed only generic $1/f$ noise, which is independent of the applied electric field, i.e., the expected scaling $S_I \propto f^2$ was obeyed. On the other hand, the Lorentzian excess noise indicates the formation of polar nanoscale regions (PNRs) that possess distinct two-level fluctuations that are dependent on the applied electric fields. The corner frequency f_c is related to the characteristic energy of the two-level fluctuator and thermally-activated states of a double-well potential with an activation energy E_a . This energy is very close to the intradimer transfer integral and optical charge gap of ~ 2900 K [4], which indicates that the observed switching processes are of electronic origin. We suggest that the competing inter- and intradimer Coulomb interactions

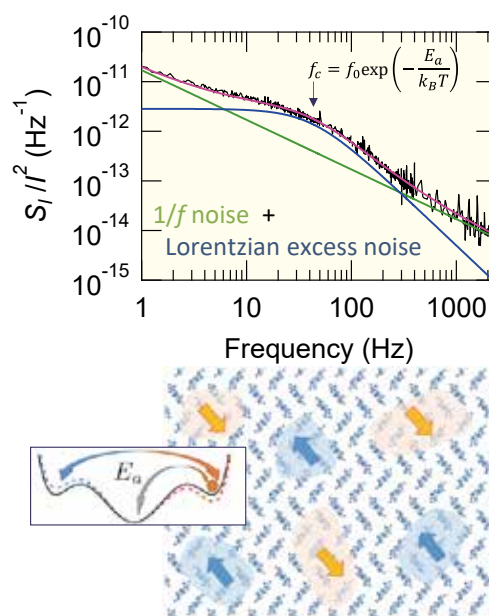


Fig. 1 shows normalized current noise PSD S_I at 130 K, which consists of $1/f$ noise and Lorentzian excess noise from ferroelectric fluctuations of PNRs (conceptual picture).

cause coherent fluctuations of electrons within a cluster of dimers, switching between the unpolarized dimer-Mott state and a charge-disproportionated state, as indicated by the bottom figure in Fig. 1.

These findings demonstrate that conductance noise spectroscopy is a sensitive tool for probing PNR formation or fluctuating mesoscopic domains and their coupling to electric fields to study the physics of materials that give rise to electronic ferroelectricity.

References

- [1] S. Iguchi, S. Sasaki, N. Yoneyama, H. Taniguchi, T. Nishizaki, and T. Sasaki, Phys. Rev. B **87**, 075107 (2013).
- [2] Y. Hattori, S. Iguchi, T. Sasaki, S. Iwai, H. Taniguchi, and H. Kishida, Phys. Rev. B **95**, 085149 (2017).
- [3] J. Müller, S. Iguchi, H. Taniguchi, and T. Sasaki, Phys. Rev. B **102**, 100103(R) (2020).
- [4] K. Hashimoto, R. Kobayashi, H. Okamura, H. Taniguchi, Y. Ikemoto, T. Moriwaki, S. Iguchi, M. Naka, S. Ishihara, and T. Sasaki, Phys. Rev. B **92**, 085149 (2015).

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Probing the Spin Current Carrier through Polarized Neutron Scattering

In insulating magnets, the spin current (i.e., flow of the spin degree-of-freedom in matter) can be propagated by the precessional motion of ordered magnetic moments. This motional direction, i.e., magnon polarization, is a unique and important signature of magnets, yet hitherto eluded experimental observations. Here, we present the first observation of magnon polarization on yttrium iron garnet through polarized neutron scattering.

The spin current in insulators can be carried by the precessional motion of ordered magnetic moments. According to the Landau–Lifshitz equation, a magnetic moment precesses counter-clockwise around the effective magnetic field direction. This motion can be described as “positively” polarized. The collective excitations in single-domain ferromagnets also precess counter-clockwise; hence, all ferromagnetic magnons have a positive polarization (Fig. (a)). Simple collinear antiferromagnets have two magnon modes with opposite polarization (Fig. (b)), but these degenerate unless large magnetic fields or Dzyaloshinskii–Moriya interactions are turned on.

Simple ferrimagnets have two anti-aligned sublattices and support two magnon polarizations; however, the intersublattice exchange field naturally separates the branches of opposite polarization into acoustic and optical modes (Fig. (c)). The energy gap between these modes can be large. Spectroscopic studies have the potential to observe this characteristic; however, there is no direct experimental proof of the magnon polarization.

We observed the magnon polarization on yttrium iron garnet $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) [1]. YIG is a ferrimagnetic insulator with a complex crystal structure, and is a quintessential magnet for spintronics and magnonics. To detect the magnon polarization, neutron spins were aligned parallel or antiparallel to the scattering wave vector ($\mathbf{Q}$). Magnetic neutron scattering can only detect the spin components perpendicular to $\mathbf{Q}$. These projections are supposed to be tiny because applied magnetic fields also align the moments along this direction. The component detected by this configuration corresponds to the area covered by the precessional motion. The use of the chiral term in polarized neutron scattering can distinguish between clockwise and counter-clockwise motion. YIG is a good material to attempt such measurements because it has a sufficiently large moment. Figure

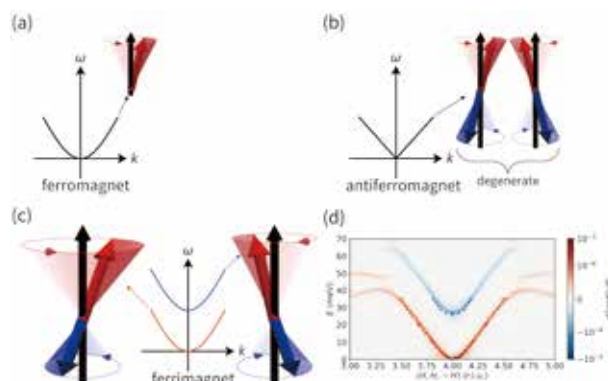


Fig. Sketch of polarization for (a) a ferromagnet, (b) an antiferromagnet, and (c) a ferrimagnet. (d) Calculated scattering cross-sections overlaid with experimentally estimated peak positions.

(d) shows the observed neutron scattering spectra. Together with theoretical calculations, magnon polarization for positive and negative signs is clearly observed for the acoustic and optical mode, respectively.

We observed the magnon polarization in the collinear ferrimagnet. The magnon polarization is directly related to the propagation direction of the spin current. Our experimental findings provide momentum/energy-resolved information on the propagation. The method we developed can be applied to more complex magnets to obtain additional microscopic views of magnetism.

References

- [1] Y. Nambu, J. Barker, Y. Okino, T. Kikkawa, Y. Shiomi, M. Enderle, T. Weber, B. Winn, M. Graves-Brook, J. M. Tranquada, T. Ziman, M. Fujita, G. E. W. Bauer, E. Saitoh, and K. Kakurai, *Phys. Rev. Lett.* **125**, 027201 (2020).

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Electric Current Control of Spin Helicity in an Itinerant Helimagnet

In a helimagnet, the ordered direction of the spin moment rotates along the wave vector. The sense of rotation, which is denoted as helicity, can be viewed as an internal degree-of-freedom when the crystal structure has inversion symmetry. We successfully controlled the helicity in an itinerant helimagnet MnP.

In a helimagnet, the helical structure hosts the chirality because any mirror operation reverses the sense of rotation, referred to as helicity. The helicity degree-of-freedom is robust against disturbances and is therefore useful for retaining information. Recently, spintronics based on antiferromagnets has attracted much attention because of its high-speed dynamics and robustness against stray fields. The helical magnetic structure is one form of antiferromagnetic structure that seems to share the characteristics mentioned above. Realization of control and helicity detection could pave way for new possibilities of magnetic memory applications based on helimagnets.

It is of great interest to understand how the spin-rotation direction couples with electromagnetic fields. In insulators, the spiral magnetic structure often induces ferroelectric polarization, as studied in the field of multiferroics. Nevertheless, the coupling between the spin-rotation direction and electric current in itinerant spiral magnets remains unknown. Theoretical work has suggested that electric current along the propagation vector induces finite magnetization in helimagnets owing to the damping torque, and that the magnetization direction depends on the helicity [1]. Based on these results, we conjecture that the degeneracy relevant to helicity should be lifted by the simultaneous application of a magnetic field and electric current.

In this work, we experimentally confirmed the conjecture [2]. To increase the electric current density, we fabricated a micrometer-scale single-crystalline sample of the helimagnet MnP using a focused ion-beam technique. We applied a large electric current j_p parallel or antiparallel to the magnetic field H_p in the high magnetic state of the fan-type magnetic structure (see Fig. 1). Then, we decreased the magnetic field below the transition field to the conical magnetic state (tilted helical magnetic state). Finally, we turned off the electric current. To probe the helicity, we measured the magnetic field dependence of the second harmonic resistivity. The field-odd component corresponds to the electrical nonreciprocity, whose sign reflects the helicity. Figure 2 shows the second harmonic

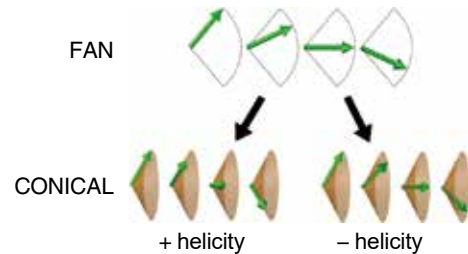


Fig. 1 Illustrations of magnetic transition from fan to conical magnetic structure. Helicity degree-of-freedom exists in the conical magnetic state but is absent in the fan magnetic structure [2].

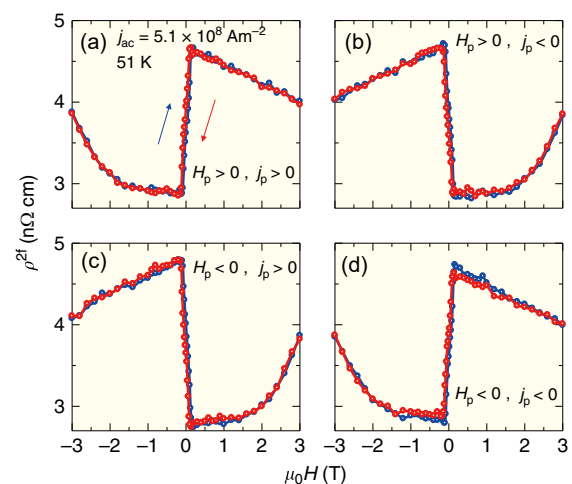


Fig. 2 (a)–(d) Magnetic field dependence of the second harmonic resistivity ρ^{2h} after the poling procedure with the positive and negative magnetic fields H_p and dc electric currents j_p [2].

resistivity after the poling procedures with positive and negative j_p and H_p . The sign of the field-odd component depends on whether j_p and H_p are parallel or antiparallel. This result demonstrates the conjectured helicity control with a magnetic field and electric current.

References

- [1] O. Wessely, B. Skubic, and L. Nordström, *Phys. Rev. B* **79**, 104433 (2009).
- [2] N. Jiang, Y. Nii, H. Arisawa, E. Saitoh, and Y. Onose, *Nat. Commun.* **11**, 1601 (2020).

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Red-Emission Scintillator Exploration

Scintillators with emission bands in the red or near-infrared region are novel materials with several important applications. We explored such materials and discovered their outstanding properties. Several cameras have been developed with these materials for applications such as a dose monitor used in extremely high radiation-dose conditions.

Scintillators are widely used in radiation detectors coupled with photosensors, such as a photodiode and photomultiplier tube. Under extremely high radiation-dose conditions, conventional photosensors can be damaged immediately owing to the ionization of semiconductors or circuits. The decommissioning of the Fukushima Daiichi nuclear plant is a major challenge, and optical fibers and scintillators are used to conduct internal surveys of the dose ratio and to identify the distribution of nuclear debris.

In such applications, the length of the optical fiber should be approximately 100 m, and effective light output (intensity) through the fiber is an important factor. The transition loss of red or near-infrared photons is lower compared with shorter wavelength photons in the optical fiber. Moreover, a large number of scintillation and Cherenkov photons can be generated by such high-dose radiation in the fiber as a noise, which are expected to dominate in a shorter wavelength region (below 600 nm).

Conventional scintillators have emission wavelength regions of 200–600 nm, and typical light output of up to 60,000 photons/MeV. Impurity emissions, such as Ce-doped materials, have good quantum efficiency, while the typical emission energy is green or blue.

Light output is basically inversely proportional to bandgap energy. The gaps of most conventional scintillators with impurity emissions cannot be smaller than the energy gaps of the emission center.

Impurity-doped materials are hard to have red-emission band(s) with good quantum efficiencies because of overlapping between conduction band and the excitation level of the emission center for allowed transition. Thus, other emission mechanisms are required to realize the red scintillators.

We focus on the charge transition transfer and self-trapped exciton luminescence, which can be generated only by host materials. In general, iodide materials tend to have a small band gap energy, and host emission for iodides tend to have a longer

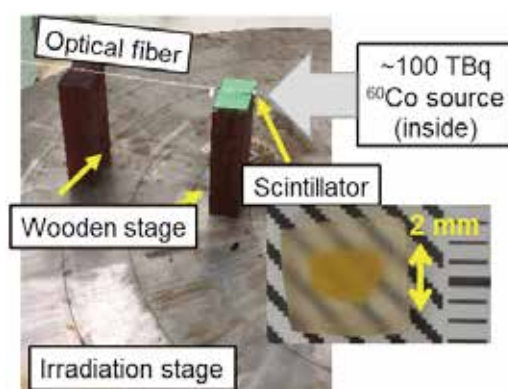


Fig. 1. Photograph of setup for demonstration test of the monitor with red-emission scintillator

wavelength.

The scintillation properties of several iodide materials, such as A_2HfI_6 , were investigated by the Bridgman method. For example, Cs_2HfI_6 has an emission wavelength of ~ 700 nm and light output of over 60,000 photons/MeV. However, the transmittance was poor ($< 50\%$) because of the low quality of raw materials (99.9%) [1]. We also successfully grew several novel crystals and crystal structures, and investigated their scintillation properties [2–3].

Because these samples have a hygroscopic nature, a piece was embedded in optical cement, as shown in Fig. 1. In addition, a real-time remote gamma-ray-dose monitor for extremely high radiation-dose conditions was developed. We successfully tested the monitor using a long optical fiber and gamma-ray source with a radioactivity of approximately 100 TBq (Fig. 1) [1].

References

- [1] S. Kodama, S. Kurosawa, and A. Yoshikawa *et al.*, Appl. Phys. Express **13**, 047002 (2020).
- [2] S. Kodama, S. Kurosawa, and A. Yoshikawa *et al.*, IEEE T NUCL SCI **67**(6), 1055 (2020).
- [3] S. Kodama, S. Kurosawa, and A. Yoshikawa *et al.*, Opt. Mater. **106**, 109942 (2020).

Keywords: scintillator, radiation imaging, crystal growth

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Thermalization Dynamics of Photo-Excited Resonantly Bonded PbTe

The ultrafast optical response of resonantly bonded systems should be investigated to gain a further understanding of the ultrafast amorphization of phase-change materials induced by femtosecond laser irradiation. Our recent work proposed a methodology for detecting the ultrafast thermalization dynamics of non-equilibrium electron and lattice systems relaxed into a thermal state, following the photoexcitation of resonantly bonded PbTe.

Chalcogenide phase-change materials (PCMs) have been applied to memory devices such as DVDs, Blu-ray discs, and PCRAMs owing to their reversible crystalline and amorphous phase-change properties and the sharp contrast between their optical and electrical properties. It has been reported that one of the representative PCMs, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST), can be amorphized within 10 ps after femtosecond (fs) laser excitation. However, it remains unclear whether this process is thermal or nonthermal. In PCM systems, “resonant bonding” is considered as one form of bonding that involves the linear long-range alignment of p -orbitals, which plays crucial role in the ultrafast phase-change process. To investigate such ultrafast dynamics following laser irradiation, we studied the ultrafast optical response and temperature-dependence of the optical properties of PbTe, which has a cubic lattice and resonant bonding like GST [1].

Figure 1 shows the temperature-dependence of the optical-density (OD) change of PbTe thin film deposited onto a quartz substrate in Ar atmosphere by the sputtering method. The ΔOD_T [= $\text{OD}(T) - \text{OD}(78\text{ K})$] value characterizes the degree of photo absorption. Figure 1 shows that PbTe became more “transparent” with the increase in temperature. This result can be explained from the viewpoint of resonant bonding. The enhanced atomic vibration at elevated temperature can disturb the long-range alignment of the p -orbital, which deteriorates or weakens the resonant bonding. Interestingly, the ΔOD_T ratio of ΔOD at 2.2 eV to ΔOD at 1.2 eV became a constant value of approximately 2.6 in the present temperature region.

On the other hand, after fs-laser irradiation at 78 K, the OD decreased over time. The decrease in ΔOD_p [= $\text{OD}(t) - \text{OD}(t = 0)$] at 1.2 eV was more prominent than that at 2.2 eV after irradiation. Figure 2 shows the temporal variation of the ΔOD_p ratio [= $\Delta\text{OD}_p(2.2\text{ eV}) / \Delta\text{OD}_p(1.2\text{ eV})$]. This clearly explores relaxation, i.e., the thermalization process between non-equilibrium electron and lattice systems toward a thermal state. In the case of PbTe, the ΔOD_p ratio

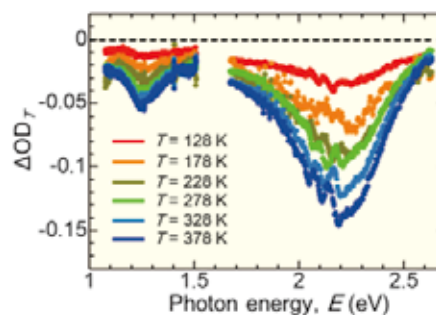


Fig. 1 The temperature-dependence of OD relative to 78 K. The ratio of ΔOD (2.2 eV) to ΔOD (1.2 eV) becomes constant of 2.6 in all temperature regions studied.

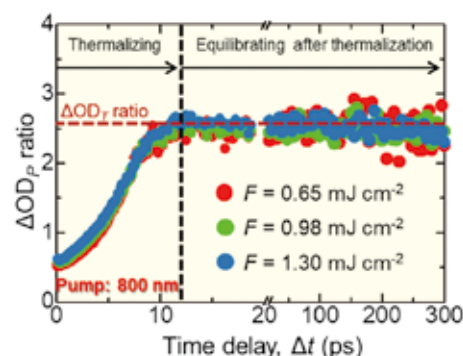


Fig. 2 The time evolution of ΔOD ratio after photo-excitation at 78 K. In the region where ΔOD is less than 2.6, electron and lattice systems are not in equilibrium.

reached 2.6 at 12 ps after photoexcitation. At this point, the system may be regarded as reaching a thermal state and that its temperature can be well defined.

Summing up, we proposed a methodology to determine the time domain for thermalization after photoexcitation. Our results provide a further understanding of the photo-induced dynamics of PCMs.

References

- [1] H. Tanimura, S. Watanabe, and T. Ichitsubo, *Adv. Funct. Mater.* **30**, 3003932 (2020).

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Alchemy for Magnets: CO₂ Switches Magnetism

Switchable magnets, with magnetic properties that can be reversibly changed in response to external stimuli, have promising potential for applications such as switches, memories, and sensors. Here, we report a gas-responsive magnet, i.e., a paramagnet on CO₂ adsorption (with its magnetism "switched off") and transforms into a ferrimagnet on CO₂ desorption (with its magnetism "switched on").

Metal–organic frameworks (MOFs), with their diverse designability and high porosity, could be ideal for gas-responsive materials. From the perspective of magnetic materials, MOFs are expected to change their magnetic properties depending on the presence or absence of guest molecules in the pores. However, obtaining selective and drastic magnetic responses to the sorption of common gases, such as O₂ and CO₂, remains challenging because the interactions between common gases and MOFs are often very weak. An effective method to induce a drastic magnetic phase change is to use our proposed magnetic changing mechanism, that is, manipulating the electronic state modulation in strongly correlated electronic systems [1,2].

A layered magnetic MOF, consisting of trifluorobenzoate-bridged paddlewheel-type ruthenium (II) dimers as electron donors (D) coordinated in-plane to 2,5-diethoxy-7,7,8,8-tetracyanoquinodimethane (TCNQ(OEt)₂) units as electron acceptors (A) in a D₂A formula, shows ferrimagnetic ordering at $T_c = 110$ K through a one-electron-transferred form of $[D-A-D^+]_\infty$ (Figs. 1a and 2a) [3]. The magnetic ordering is attributed to the strong superexchange interactions between the paramagnetic D ($S = 1$ for a $[Ru^{II}, Ru^{II}]$ cluster) and D^+ ($S = 3/2$ for a $[Ru^{II}, Ru^{III}]^+$ cluster) subunits via A^- with $S = 1/2$ (TCNQ(OEt)₂^{•-}) (Fig. 1a). When CO₂ is adsorbed in a stepwise manner within and between layers, the $[D-A-D^+]_\infty$ framework undergoes stepwise structural transitions, with the second transition involving an intralattice electron transfer ($D^+ \leftarrow A^-$) to produce a paramagnetic neutral form of $[D-A-D]_\infty$ with diamagnetic A (Figs. 1b and 2a).

In addition to magnetism, this sudden electron transfer involving CO₂ uptake/release induces modulations of electronic conductivity (Fig. 2b) and permittivity, revealing a favorable example of the feasibility and versatility of MOFs for guest molecules. Theoretical calculations using density functional theory suggest that accommodated CO₂ molecules have significant electronic interactions with the framework. These findings provide insights

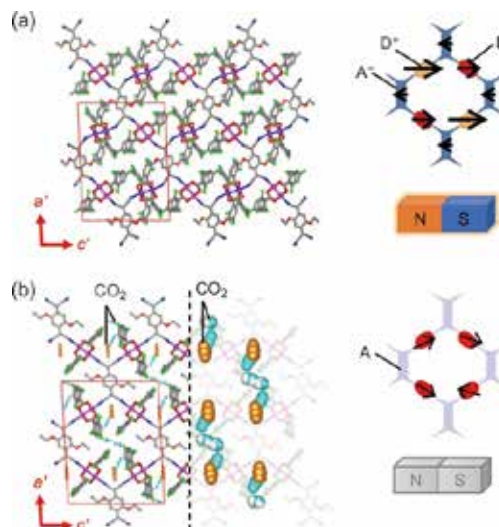


Fig. 1 Crystal structures of layered magnetic MOF without gas (a) and within CO₂ (b).

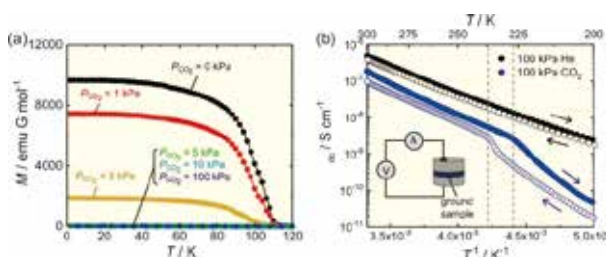


Fig. 2 (a) The CO₂ pressure-dependence of field-cooled magnetization curves at $H_{dc} = 100$ Oe. (b) Temperature-dependence of σ_{dc} measured on a pelletized sample under $P = 100$ kPa of He (black) and CO₂ (blue).

into the mechanism by which switchable properties can be controlled by gas sorption, which may be helpful in future applications, such as gas sensors or memory storage.

References

- [1] J. Zhang, W. Kosaka, K. Sugimoto, and H. Miyasaka, *J. Am. Chem. Soc.* **140**, 5644 (2018).
- [2] J. Zhang, W. Kosaka, Y. Kitagawa, and H. Miyasaka, *Angew. Chem. Int. Ed.* **58**, 7351 (2019).
- [3] J. Zhang, W. Kosaka, Y. Kitagawa, and H. Miyasaka, *Nat. Chem.* **13**, 191 (2021).

Keywords: crystal structure, magnetic properties, porosity

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Highly Ordered L1₀-FeNi Films with Large Uniaxial Magnetic Anisotropy Fabricated by a Denitridding Method

L₁₀-ordered FeNi alloy is a candidate material for applications in rare-earth-free and noble-metal-free permanent magnets and magnetic storage technology. This paper reveals that denitridding FeNiN films is an effective method to form L₁₀-ordered FeNi films with a high degree of order and a large uniaxial magnetic anisotropy energy.

Ferromagnetic materials that possess large uniaxial magnetic anisotropy energy (K_u) and consist of earth-abundant elements are required to realize the next-generation permanent magnets and magnetic storage. An L₁₀-ordered FeNi alloy has been considered as a rare-earth-free high K_u material [1]. Recently, the synthesis of polycrystalline L₁₀-FeNi powder by denitridding FeNiN powder was reported (Fig. 1), and a high degree of order (S) of 0.71 was achieved [2]. However, the exact K_u value of L₁₀-FeNi formed by the denitridding method remains unclear. The preparation of a single-crystal L₁₀-FeNi is indispensable for the evaluation of K_u . In this study, epitaxial FeNiN films were grown by molecular beam epitaxy. Then, L₁₀-FeNi films were fabricated using nitrogen topotactic extraction from the FeNiN, which allowed us to quantitatively characterize their S and K_u values.

FeNiN films with a thickness of 20 nm were grown on SrTiO₃(001) substrates at 200, 250, and 350 °C by supplying Fe, Ni, and RF N₂ plasma, simultaneously [3]. Denitridding was performed by ex-situ furnace annealing at 300 °C for 4 h under a H₂ gas flow rate of 1 l/min at ambient pressure. The structure of the samples was characterized by x-ray diffraction measurements using Cu- $K\alpha$ radiation and synchrotron radiation ($h\nu = 7.11$ keV), and cross-sectional scanning transmission electron microscope (STEM) measurements. The saturation magnetization (M_s) and the K_u were estimated by magnetic torque measurements.

The epitaxial L₁₀-FeNi films oriented with the a -axis perpendicular to the film plane were fabricated, which had two variants with the in-plane c -axes orthogonal to each other. Figure 2 shows the growth temperature dependence of M_s and K_u . For the sample grown at 350 °C, the S and K_u values were evaluated as 0.87 and 5.9×10^5 J/m³, respectively. The large S exceeding those reported previously [1,2] may allow us to expect a larger K_u value. The exchange length of L₁₀-FeNi (3.2 nm) is comparable to the variant sizes of samples estimated by the STEM measurements. This suggests that the obtained macroscopic K_u value averages out owing to the exchange coupling of

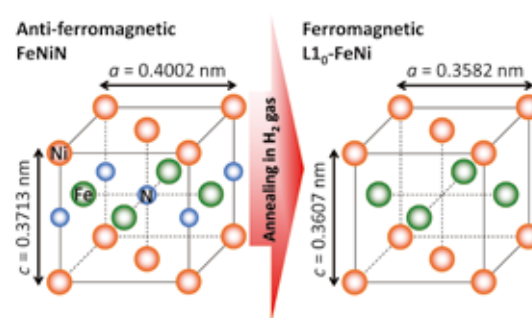


Fig. 1 Crystal structures of FeNiN and L₁₀-FeNi. L₁₀-FeNi is fabricated by topotactic extraction of N atoms from FeNiN.

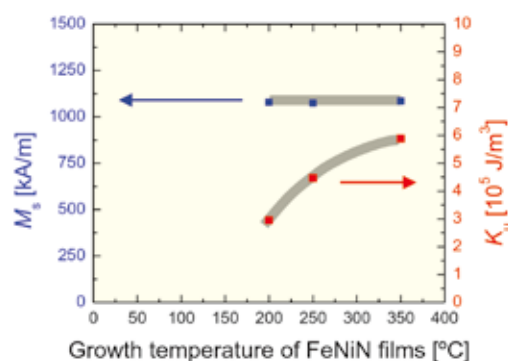


Fig. 2 Growth temperature dependence of M_s and K_u of the samples.

variants with different easy axes and is smaller than the actual K_u of each variant [4].

References

- [1] K. Takanashi, M. Mizuguchi, T. Kojima, and T. Tashiro, J. Phys. D: Appl. Phys. **50**, 483002 (2017).
- [2] S. Goto, H. Kura, E. Watanabe, Y. Hayashi, H. Yanagihara, Y. Shimada, M. Mizuguchi, K. Takanashi, and E. Kita, Sci. Rep. **7**, 13216 (2017).
- [3] K. Ito, M. Hayashida, M. Mizuguchi, T. Suemasu, H. Yanagihara, and K. Takanashi, J. Magn. Soc. Jpn. **43**, 79 (2019).
- [4] K. Ito, M. Hayashida, H. Masuda, T. Nishio, S. Goto, H. Kura, T. Koganezawa, M. Mizuguchi, Y. Shimada, T. J. Konno, H. Yanagihara, and K. Takanashi, Appl. Phys. Lett. **116**, 242404 (2020).

Keywords: magnetic properties, thin films, molecular beam epitaxy (MBE)

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Growth of a Super Uniform Congruent-Melting LiNbO₃ Crystal

A super uniform congruent-melting LiNbO₃ (cs-MgO:LN) was grown, which was simultaneously stoichiometric and congruent. The equilibrium partitioning coefficient k_0 is unity for all ionic species; therefore, the segregation of ionic species is not expected to occur during crystal growth even when cs-MgO:LN exhibits non-steady-state growth. This confirms the improved compositional stability compared with conventional LiNbO₃ under all growth conditions.

So-called “high-quality” crystals are always grown from congruent melts in which the crystal maintains exactly the same composition as that of the melt. The congruent composition is represented in a phase diagram as the intersection of the liquidus line and solidus line. Then, the equilibrium partition coefficient k_0 is unity for the components in the phase diagram. The congruent point, which is invariant with zero degrees-of-freedom, is located at the summit of the liquidus lines showing the highest temperature. Although it appears unstable, it is very stable because the congruent point is located at the lowest position of the molar free energy curves of the solid and liquid as a common tangent point. However, more care and attention is needed when dealing with the oxide melt. The oxide melt contains a variety of ionic species [1] whose k_0 s are not necessarily unity, although the k_0 s of the constituent components of the phase diagram (system components) are unity. The segregation of ionic species occurs at the interface, even for congruent growth. Interestingly, the crystal composition is always congruent during steady-state growth [1]. However, a perturbation of the heat and mass flow beneath the interface always occurs during growth, which changes the growth velocity and crystal composition. Here, we should know when the k_0 s of all ionic species are unity; their populations at the interface never change but remain constant as in the bulk melt, even if a growing crystal experiences an abrupt change in growth velocity. Thus, the crystal composition was surprisingly uniform throughout the growth. Such bulk crystals were created by doping MgO into LiNbO₃, which is referred to as cs-MgO:LN (Li₂O:Nb₂O₅:MgO = 45.30:50.00:4.70) [2]. It has a congruent point coincident with the stoichiometric composition, which makes k_0 unity for all ionic species. To construct cs-MgO:LN, we introduced the extended concept of “stoichiometry,” that is, “a material in which the activities of all the constituent elements that can be unity is stoichiometric.” This concept

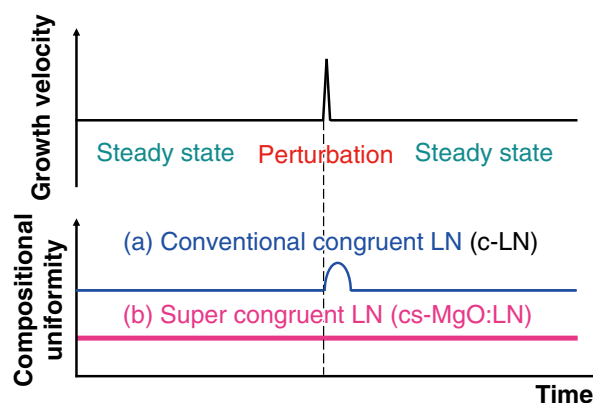


Fig. 1 Compositional stability in (a) conventional and (b) super congruent LN when confronting a growth perturbation.

expands the stoichiometric composition from a point to a line, so that coincidence with the congruent point can occur much more easily. In Fig. 1, the cs-MgO:LN crystal shows no composition fluctuations even if it confronts non-steady-state growth because it has a unity of k_0 for every chemical species, which ensures the super uniform distribution of the refractive index with $\Delta n < 10^{-5}$ /cm; this is beneficial for developing future optical devices with extremely high precision. However, conventional c-LN shows a compositional bump. In conclusion, cs-MgO:LN has a great advantage over c-LN in terms of compositional uniformity.

References

- [1] S. Uda and C. Koyama, J. Cryst. Growth **548**, 125837 (2020).
- [2] Q. Shi, J. Nozawa, and S. Uda, J. Cryst. Growth **549**, 125864 (2020).

Keywords: crystal growth, crystal structure, doping
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Multiple Superconducting Phases in Novel Spin-Triplet Superconductor UTe₂

We discovered multiple superconducting phases in the novel spin-triplet superconductor UTe₂ under a magnetic field and pressure. Owing to the thermodynamic response shown by AC calorimetry measurements, H - T phase diagrams under pressure were determined for the field along the a -axis in the orthorhombic structure. The unusual enhancement of the upper critical field H_{c2} was observed as a consequence of multiple superconducting phases. This behavior of H_{c2} requires the state of the superconducting order parameter to be more complex than the spin-triplet state with equal-spin pairing.

Heavy fermion superconductivity in UTe₂ has attracted much attention because of recently discovered superconducting phenomena. UTe₂ is a paramagnet with a heavy electronic state in the proximity of the ferromagnetic order. The microscopic coexistence of ferromagnetism and superconductivity has already been established for uranium-based compounds, namely UGe₂, URhGe, and UCoGe. The newly discovered UTe₂ has many similarities with these ferromagnetic superconductors. One of the highlights of UTe₂ and ferromagnetic superconductors is the huge superconducting upper critical field H_{c2} . In UTe₂, when the field is applied along the hard magnetization axis (b -axis), the superconducting phase persists at an extremely high field up to 35 T, which is one order of magnitude larger than usually expected at the superconducting transition temperature 1.6 K. Furthermore, the H_{c2} curve displays field re-entrant behavior; T_c at 35 T is two times higher than that at 15 T. Therefore, spin-triplet superconductivity is expected because H_{c2} can be enhanced by tuning the ferromagnetic fluctuation without the Pauli paramagnetic effect. Another important aspect of spin-triplet superconductivity is the spin degree-of-freedom. In this case, multiple superconducting phases are theoretically expected, as is well known in superfluid ³He. However, obtaining experimental evidence for multiple superconducting phases is a difficult task.

We performed AC calorimetry measurements under pressure and for the field along the easy-magnetization axis (a -axis) in UTe₂ to clarify whether the superconducting phases are a thermodynamic response. Figure 1 shows the H - T phase diagram at 0.54 GPa for the $H \parallel a$ -axis. The superconducting transition temperature was enhanced to $T_c = 2.5$ K compared with that at ambient pressure ($T_c = 1.6$ K). When the field was increased, T_c decreased with a strong convex curvature. At temperatures below 0.4 K, H_{c2} abruptly increased and reached 8 T at 0 K. This H_{c2} curve was also confirmed by magnetoresistance [2]. The Pauli limitation exhibited by H_{c2} could be attributed to the appearance of the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state, in which the pair-breaking due to the Pauli paramagnetic effect is reduced. However, this is unlikely because the FFLO state never produces the sharp kink observed in

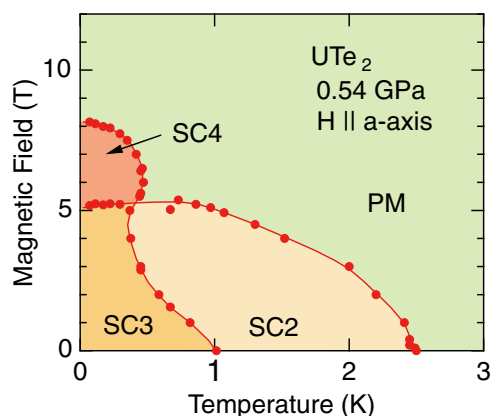


Fig. 1 H - T phase diagram for $H \parallel a$ -axis at 0.54 GPa [1]. PM, SC denote paramagnetism and superconductivity, respectively

UTe₂. Moreover, UTe₂ is a three-dimensional superconductor, different from the two-dimensional iron-based superconductor. Most importantly, the abrupt increase in H_{c2} emerged as a prolongation of the lower superconducting transition existing at zero field, where no paramagnetic limitation exists. Our results demonstrate multiple superconducting phases, which may require different order parameters for each phase. Several theoretical models to explain this phase diagram have been proposed based on the existence of point node gaps at ambient pressure indicated by field-angle resolved specific heat measurements [3].

This work was done in collaboration with F. Honda, G. Knebel, D. Braithwaite, A. Nakamura, D.X. Li, Y. Homma, Y. Shimizu, Y. J. Sato, J.P. Brison, and J. Flouquet.

References

- [1] D. Aoki, F. Honda, G. Knebel, D. Braithwaite, A. Nakamura, D.X. Li, Y. Homma, Y. Shimizu, Y. J. Sato, J. P. Brison, and J. Flouquet, *J. Phys. Soc. Jpn.* **89**, 053705 (2020).
- [2] G. Knebel, K. Motoi, M. Valiska, F. Honda, D.X. Li, D. Braithwaite, G. Lapertot, W. Knafo, A. Pourret, Y. J. Sato, Y. Shimizu, T. Kihara, J. P. Brison, J. Flouquet, and D. Aoki, *J. Phys. Soc. Jpn.* **89**, 053707 (2020).
- [3] S. Kittaka, Y. Shimizu, T. Sakakibara, A. Nakamura, D. X. Li, Y. Homma, F. Honda, D. Aoki, and K. Machida, *Phys. Rev. Res.* **2**, 032014(R) (2020).

Keywords: superconducting, heavy fermion, actinide

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Self-Organized Solid-State Epitaxy of PZT Thin Films by Chemical Solution Deposition

The film–substrate interface is critical for crystal growth via solid-state epitaxy. We have elucidated the local structure and crystallization mechanism of amorphous phase $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ ($x = 0.3$) thin films deposited onto SrTiO_3 (001) single-crystal substrates by chemical solution deposition. The amorphous phase involves a short-range order of $(\text{Ti/Zr})\text{O}_6$ octahedra and Pb-O . The first unit cells of the film have already crystallized with a cube-on-cube epitaxial relationship with the substrate.

Chemical solution deposition (CSD) is a thin film growth technique with several advantages over gas-phase processes, such as excellent composition transferability from mixed raw materials to thin films, simple facilities, and low cost. We have studied metal-organic deposition as the simplest CSD. This process involves the following steps: metal-organic precursors with long-chain organic ligands were dissolved in an organic solution, and coated by spraying, dipping, or spin coating. These were then dried to remove solvents, decomposed into an amorphous oxide thin film as a precursor, and heated to crystallize. In this CSD process, it is important to establish the structure and bonding states of amorphous oxide thin films, and the interface structure between the film and substrate, immediately after decomposition. However, the initial stage of the crystal growth mechanism using chemical solvents has not been elucidated because crystal growth cannot be monitored in real time.

Figure 1 shows the (a) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and (b) annular bright field STEM (ABF-STEM) images of the amorphous $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT) thin film after pyrolysis at 350 °C, which is considerably lower than the crystallization temperature of 650 °C [1]. The first Pb-O layer of PZT crystallized coherently, while the second Pb-O layer showed a weaker contrast.

These results correspond to a situation in which the first Pb-O layer widely covers the SrTiO_3 surface, while the second layer covers it locally, and the interplane distance increased. Figure 1(b) shows the incorporation of atoms in the second Pb-O layer.

Figure 2(a) shows the Ti-L_{23} electron energy loss near-edge structures (ELNES) of the amorphous phase, interface layer, tetragonal phase, and rhombohedral phase of PZT thin films [1]. The pyrolyzed films show ligand field splitting under O_h local symmetry, that is, the TiO_6 octahedron coordination structure already exists in the pyrolyzed

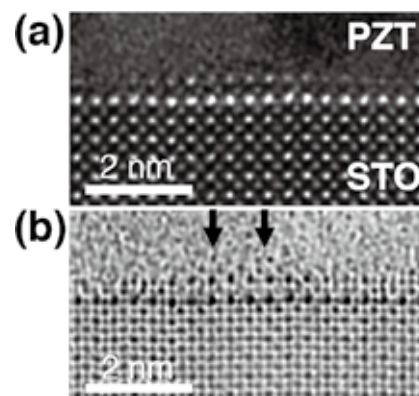


Fig. 1 (a) HAADF- and (b) ABF-STEM images of the amorphous PZT thin film. Arrows point out just incorporating atoms on the second Pb-O layer.

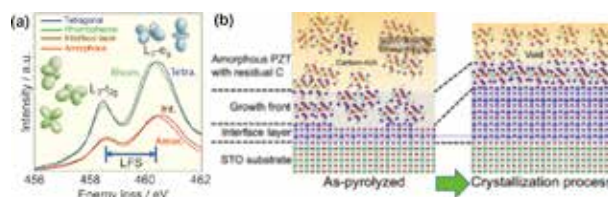


Fig. 2 (a) Ti-L_3 ELNES of amorphous phase, interface layer, tetragonal phase, and rhombohedral phase of PZT thin films. (b) Schematic model of the crystallization process of the amorphous PZT thin film.

PZT thin film, which is apparently an amorphous phase, as shown in Fig. 1. These results indicate that the amorphous PZT thin film has a short-range order and was incorporated into the crystalline films via interface layers as self-organized nucleation sites (Fig. 2(b)).

The present study demonstrates that the interface layer and short-range order in amorphous films are among the essential factors governing the solid-state epitaxy of oxides by CSD.

References

- [1] T. Kiguchi, T. Shimizu, T. Shiraishi, and T. J. Konno, *J. Ceram. Soc. Jpn.* **128**, 501 (2020).

Keywords: thin films, epitaxial growth, electron microscopy

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Dynamics of Absorption/Emission of Hydrogen Isotope in Neutron-Irradiated Tungsten with the Compact Divertor Plasma Simulator

International Research Center for Nuclear Materials Science

A compact divertor plasma simulator combined with thermal absorption spectroscopy was developed in the radiation-controlled area of the IRCNMS. The dynamics of hydrogen isotope absorption/emission for neutron-irradiated tungsten are being investigated, which will be essential for ongoing studies on plasma-facing materials in fusion reactors.

Studies on fusion reactors are ongoing worldwide. These include the development of plasma-facing materials that requires an understanding of hydrogen isotope behavior in the materials. Systematic experiments on the absorption/emission of hydrogen isotopes in neutron-irradiated materials are of importance for this matter, but few are available worldwide.

Recently a compact divertor plasma simulator (CDPS), as shown in Fig. 1, was developed in the radiation-controlled area of the International Research Center for Nuclear Materials Science (IRCNMS), Tohoku University, as a result of collaborations with the National Institute for Fusion Science and other universities [1]. The CDPS produces steady-state deuterium (D) and/or helium plasmas with densities above 10^{18} m^{-3} at a well-controlled sample temperature of approximately 5 K. The CDPS has a sample-carrier system, which makes it possible to transfer a plasma-exposed sample from the sample holder to an infrared heater for analysis using thermal desorption spectroscopy, without exposing it to the air.

We performed neutron-irradiation for tungsten, which is the primary candidate for plasma-facing material. Then, we investigated the dynamics of D absorption and emission [2, 3]. The total D retention was found to be proportional to the square root of D fluence, as shown in Fig. 2. The results suggest that the implanted D atoms first occupied the defects near the surface, and then the defects located in deeper regions. The effects of post-plasma annealing on D emission was also studied. It was found that 30 h of annealing at 573 K caused D emissions, suggesting that the heat treatment of the plasma-facing component of a fusion reactor at moderately elevated temperatures can contribute to the removal of accumulated hydrogen isotopes. These results were obtained through international collaborations at the IRCNMS and will be essential for ongoing and future studies of plasma-facing materials in fusion reactors.

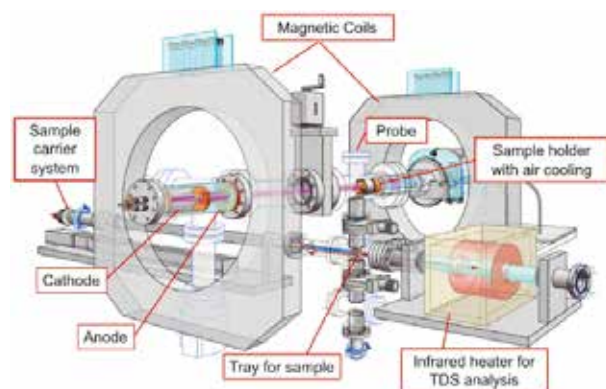


Fig. 1 Schematic view of the CDPS.

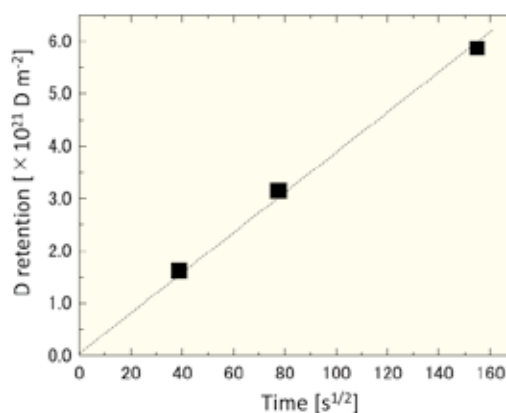


Fig. 2 Correlation between the plasma exposure time and D retention in neutron-irradiated pure tungsten.

References

- [1] N. Ohno, T. Kuwabara, M. Takagi, R. Nishimura, M. Yajima, A. Sagara, T. Toyama, K. Suzuki, H. Kurishita, T. Shikama, Y. Hatano, and N. Yoshida, *Plasma Fusion Res.* **12**, 1405040 (2017).
- [2] V. Kh. Alimov, Y. Hatano, T. Kuwabara, T. Toyama, S. Someya, and A. V. Spitsyn, *Nucl. Fusion* **60**, 096025 (2020).
- [3] T. Toyama, M. Yajima, N. Ohno, T. Kuwabara, V. Kh. Alimov, and Y. Hatano, *Plasma Fusion Res.* **15**, 1505081 (2020).

Keywords: nuclear materials, radiation effects, hydrogen

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Photoactivity of an Anodized Biocompatible TiNbSn Alloy

Cooperative Research and Development Center for Advanced Materials

A bioactive TiNbSn alloy was anodized in an electrolyte of sodium tartrate containing hydrogen peroxide (H_2O_2). Highly crystallized porous rutile-structured TiO_2 that formed on TiNbSn exhibited superior photoactivity and generated hydroxyl radicals under ultraviolet illumination. The photoactivity was attributed to the highly crystallized TiO_2 formed by the application of a high voltage during anodization, thus suppressing the recombination of the photogenerated carriers.

Metallic implant materials can release metallic ions into biological fluids and tissues, causing allergies and possibly granuloma formation. Abraded micron-sized wear particles can also cause fretting, impinging inflammatory reactions, and eventual bone resorption through their accumulation in surrounding tissues following long-term exposure to the biological environment or transport to distant organs by synovial fluid, blood, or urine. Thus, the demand for biocompatible surface coatings on metal implants has increased.

Figure 1(a) shows the plots of the photoactivity (degradation rate of methylene blue) against the average amount of $\bullet\text{OH}$ generated upon ultraviolet illumination (measured by electron spin resonance) for as-anodized and annealed anodic oxides on Ti and TiNbSn. Two separate regions could be contoured for the anodic oxides on Ti and TiNbSn, respectively. This result indicates that the photogenerated electrons to generate $\bullet\text{OH}$ were not transferred to H_2O_2 for TiO_2 on Ti, and transferred to H_2O_2 for rutile TiO_2 on TiNbSn, and is related to the defects in TiO_2 inducing charge recombination [1].

The highly crystallized rutile TiO_2 contains a low

density of defects owing to self-heating during anodization, which is attributed to the high electric resistivity of the TiNbSn alloy. Galvanostatic anodization increased the voltage due to the high resistivity of the alloy, and micro-arc oxidation and spark discharge associated with oxide dissolution occurred. As a result, porous anodic oxide with a rough surface was formed on TiNbSn alloy. Depth analysis by glow discharge optical emission spectroscopy revealed the presence of alkaline metals Na and K originating from the electrolyte near the interface between the oxide and TiNbSn alloy. This suggests that these alkaline metals were incorporated into the oxide after adsorption to the surface of the TiNbSn alloy.

It was concluded that the application of a high voltage promoted anodization, resulting in the formation of well-crystallized porous TiO_2 and the improvement of photocatalytic activity.

References

- [1] N. Masahashi, Y. Mori, H. Kurishima, H. Inoue, T. Mokudai, S. Semboshi, M. Hatakeyama, E. Itoi, and S. Hanada, *Appl. Surf. Sci.* **543**, 148829 (2021).

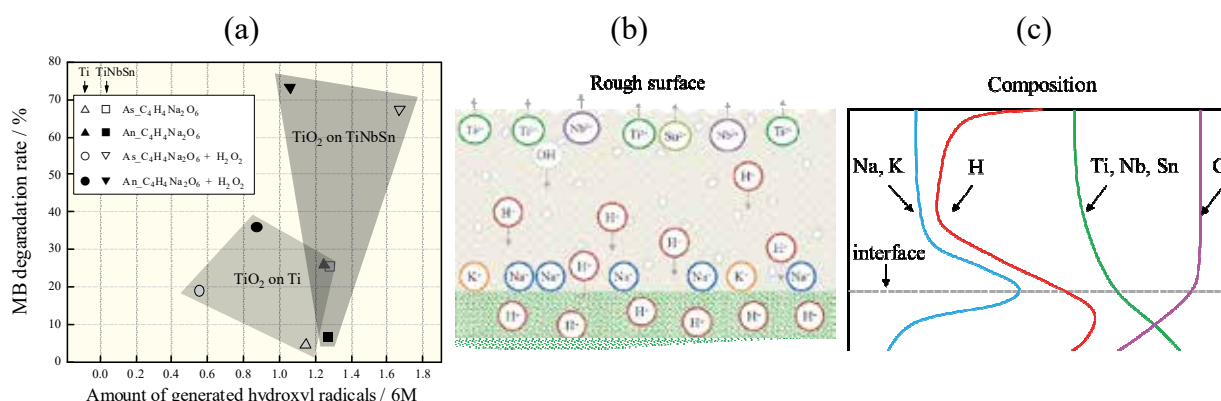


Fig. 1 (a) Plots of the degradation rate of MB against the amounts of generated $\bullet\text{OH}$ upon UV illumination for as-anodized and annealed anodic oxides on Ti and TiNbSn. (b) Schematic structural and (c) compositional illustration of the evolution of anodic oxide on TiNbSn [1].

Keywords: biomaterial, oxide, photocatalytic

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Magnetization of YBCO and MgB₂ Bulks Under High Magnetic Fields

High Field Laboratory for Superconducting Materials

High magnetic field trapping has been studied for Y-Ba-Cu-O (YBCO) and MgB₂ superconducting bulks. We achieved the high magnetic field trapping of 15.1 T in YBCO bulks and 5.58 T in Ti-doped MgB₂ bulks by the field-cooled magnetization method. The trapped field of 5.58 T is a world record among MgB₂ bulk magnets.

High-temperature superconducting (HTS) bulk magnets can be used as a quasi-permanent magnet. In particular, they can trap very high magnetic fields that cannot be obtained by conventional permanent magnets. High-field HTS bulk magnets have novel superconducting applications, such as a compact bench-top NMR/MRI. The trapped magnetic field is limited by the critical current density J_c , the mechanical strength, and the superconducting stability of bulk materials.

The stacking of the Y-Ba-Cu-O (YBCO) superconducting bulk-pair reinforced by a stainless steel (SUS) container was magnetized by field-cooled magnetization (FCM) under magnetic fields of up to 22 T using the 28 T hybrid magnet (28T-HM). Numerical simulations were used to optimize the structure of the SUS container against the electromagnetic hoop stress of approximately several hundred MPa. We obtained the trapped magnetic field of 15.1 T by FCM from 18 T at 28 K at the center of the YBCO pair, as shown in Fig. 1. However, cracking partially occurred at the periphery of both YBCO bulks during FCM from 22 T at 23 K. The bulk fracture originated from the thermal shock by the flux jumps [1].

Ti-doped MgB₂ bulks were prepared by a hot isostatic pressing method. We succeeded in the high-field trapping of 5.58 T by FCM from 6 T at 11.3 K for the triple-stacking Ti-doped MgB₂ bulks [2]. We found that the Ti-doped MgB₂ bulks had the ability to trap a 7 T class magnetic field at temperatures below 4.2 K, as shown in Fig. 2; however, the FCM experiments at both 2.2 and 4.2 K were disturbed by flux jumps.

The experimental results suggest that thermal instability triggered the large-scale vortex jumps and large heat generation. Hence, it is important to improve the thermal stability of the bulks to realize a stronger trapped field magnet.

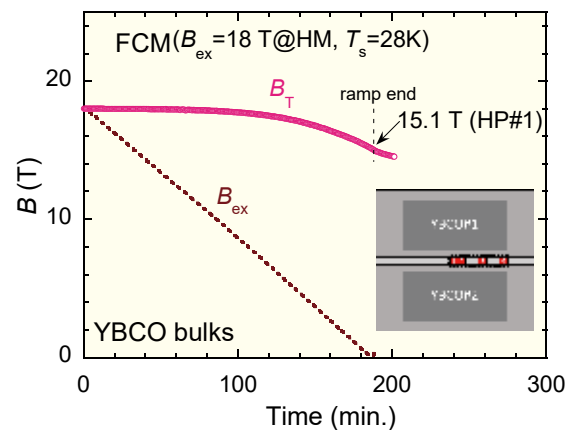


Fig. 1 The field trapping process during FCM from 18 T at 28 K for the YBCO bulk pair.

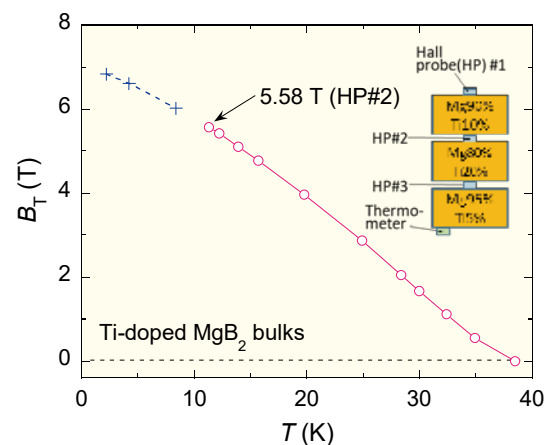


Fig. 2 Temperature-dependence of the trapped field for the triple-stacking Ti-doped MgB₂ bulks.

References

- [1] T. Naito, H. Fujishiro, and S. Awaji, J. Appl. Phys. **126**, 243901 (2019).
- [2] T. Naito, Y. Takahashi, and S. Awaji, Supercond. Sci. Technol. **33**, 125004 (2020).

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Scientific Breakthrough Toward Creation of New Industrial Materials

Trans-Regional Corporation Center for Industrial Materials Research

The Institute for Materials Research (IMR) has launched the Trans-Regional Corporation Center, a comprehensive institute-wide effort that pairs research groups at IMR across the innovation spectrum to solve current industrial problems and prepare for future global energy problems. The Center was established in 2016 by an agreement between IMR, the Osaka Prefecture government, and enterprises in the Kansai area sponsored by government; it took over Osaka and Kansai center projects.

In April 2016, the Trans-Regional Corporation Center was established in Osaka as a special unit of the Institute for Materials Research (IMR), Tohoku University, as a result of an agreement with the Osaka Prefecture government. The Center is sponsored by the Ministry of Education, Culture, Sports, Science and Technology, which took over the Kansai Center and carried out its mission from 2012 to 2016. The Center has three missions. First, to solve technical problems that industries have struggled with. Second, to introduce academic output to industries for application to society. Third, to help educate next-generation materials scientists and researchers in universities and enterprises. The Center organized the forum “Monodukuri Kisokoza,” which focuses on special topics in materials and processing. Projects are conducted through collaborations with the government, universities, research institutions, and other organizations. The Center has four venues to cover the Kansai area: the Osaka office at Osaka Prefecture University, the Hyogo office at University of Hyogo, the Sendai office in IMR, and Monozukuri Business Information Center Osaka in the Creation Core Higashi-Osaka.

The Center has developed materials and processes in collaboration with industries. These include a thermal-sprayed amorphous magnetostrictive film developed by IMR and USUI Co., LTD. New magnetic amorphous alloys with a high glass-forming ability have been developed, such as the (Fe, Co)-Si-B-Nb alloy. Amorphous alloys are known to exhibit low coercivity, although their magnetostriction is relatively large. Some properties of amorphous magnetostrictive films with high glass-forming ability and the constitution of the torque sensor have been investigated. The amorphous (Fe, Co)-Si-B-Nb spraying films with high adhesion strength were formed on the surface



Fig. 1 (a) The shaft for rotating-torque sensor with thermal-spraying film of (Fe, Co)₇₂Si₄B₂₀Nb₄ amorphous alloy, and (b) the developed product of the rotating-torque sensor.

of the shaft using a spray-quenching system and by controlling the substrate temperature (Fig. 1(a)). The shaft developed with the amorphous thermal sprayed alloy generated an output voltage five times higher compared with the Fe shaft machined into the surface morphology of the chevron pattern [1]. These products of the torque sensor (Fig. 1(b)), which assembled the shaft with the spraying films, have excellent sensor properties, such as high sensitivity and low hysteresis measurement error [2].

Similar collaborative research for practical applications utilizing academic knowledge and industrial technology are in progress. The Center will make an effort to innovate in the metallic material industry through alliances and by promoting research on materials science.

References

- [1] M. Komaki, H. Ashino, S. Kamata R. Tsunemi, Y. Saotome, and K. Amiya, Japan Patent, 5940531-B2, 2016-5-27.
- [2] Tohoku Techno Arch Co., Ltd., *Success Stories*, https://www.t-technoarch.co.jp/content/licence_T12-094.html (15. Nov. 2020)

Keywords: metallic glass, magnetic properties, devices

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Comparison of Spin and Polarization Caloritronics

Collaborative Research Center on Energy Materials

The spontaneous order of electric and magnetic dipoles in ferroelectrics and ferromagnets, even at high temperatures, is both fascinating and useful. Spintronics studies the transport of magnetic order in the form of spin currents, but the polarization current of the ferroelectric order has escaped attention. We present a time-dependent diffusion theory for heat and polarization transport in a planar ferroelectric capacitor with parameters derived from a one-dimensional phonon model. We predicted the steady-state Seebeck and transient Peltier effects.

Ferromagnetism and ferroelectricity describe the order of magnetic and electric dipoles that spontaneously form, often far above room temperature and have much in common [1]. The robustness of the order and the associated stray magnetic and electric fields give rise to numerous technological applications that affect our daily lives. However, the physics appears to be very different. The Amperian electric (Gilbertian magnetic) dipoles break the (conserve) inversion symmetry but conserve the (break) time-reversal symmetry. Nevertheless, the phenomenology of these material classes displays similar analogies. The dipolar order is staggered in antiferromagnets and antiferroelectrics. The electrocaloric (magnetocaloric) effect is based on the dependence of the entropy of electric (magnetic) dipolar ensembles as a function of the applied electric (magnetic) field and temperature [2]. Both the magneto- and electrocaloric heat pumps appear to be close to the market. However, an equivalent for spin caloritronics [3] in ferroelectric materials does not exist.

Motivated by the need to find new uses for ferroelectric materials in energy applications and supported by the co-appointment scheme between NIMS and Tohoku University, we studied the caloritronics of ferroelectric capacitors [4], i.e., ferroelectric insulators sandwiched between two metal contacts.

The linear response relation in a *ferromagnetic* insulator (Ohm's law) is as follows [3]:

$$\begin{pmatrix} J_s \\ J_q \end{pmatrix} = G \begin{pmatrix} 1 & ST \\ \Pi & K/G \end{pmatrix} \begin{pmatrix} \Delta H \\ \Delta T \end{pmatrix}, \quad (1)$$

where J_s is the spin current, J_q is the heat current, G is the spin conductance, T is the temperature, S is the Seebeck coefficient, Π is the Peltier coefficient, K the heat conductance ΔH is the magnetic field difference, and ΔT is the temperature difference between the devices. For a *ferroelectric* insulator, the equation is almost the same [4].

$$\begin{pmatrix} J_p \\ J_q \end{pmatrix} = G \begin{pmatrix} 1 & ST \\ \Pi & K/G \end{pmatrix} \begin{pmatrix} \Delta E \\ \Delta T \end{pmatrix}, \quad (2)$$

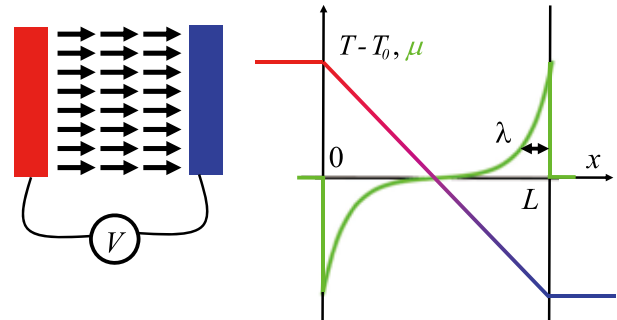


Fig. 1 A temperature gradient over a ferroelectric capacitor (left) drives a polarization current. For opaque interfaces, this leads to polarization accumulation μ on the scale of the diffusion length λ . The latter may generate an observable thermovoltage V .

However, the spin current is replaced by a polarization current, the drive is an electric instead of a magnetic field difference, and the material constants have other units.

Excited magnetic or electric polarizations are not conserved but characterized by material-dependent lifetimes. In diffusion approximation, this leads to spin (or magnon) accumulation in magnets and polarization accumulation in ferroelectrics, parameterized by non-equilibrium chemical potentials. The solution of the diffusion equation shows that the accumulations exist near interfaces on the scale of the diffusion length λ , as shown in Fig. 1. The spin diffusion length can be tens of micrometers in yttrium iron garnets, but there is no data on ferroelectrics. In the absence of experiments, we estimated the model parameters using a simple one-dimensional phonon model of elastically coupled electric dipoles [4].

References

- [1] N. A. Spaldin, *Topics Appl. Phys.* **105**, 175 (2007).
- [2] S. Crossley et al., *AIP Advances* **5**, 067153 (2015).
- [3] G.E.W. Bauer, E. Saitoh, and B.J. van Wees, *Nature Mat.* **11**, 391 (2011).
- [4] G.E.W. Bauer, R. Iguchi, and K. Uchida, *Phys. Rev. Lett.*, (2021) in press.

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Unique Power-Law Scaling in Nanoindentation Pop-ins

Center for Computational Materials Science

Power laws are obeyed in many scientific fields, including the plasticity of materials. Large-scale molecular dynamics nano-indentation simulation and nano-indentation testing showed that the power law statistics in the displacement burst (pop-in) magnitude of the nano-indentation is unique. Thus, the power law exponents are much higher than those typically observed in plasticity.

Power laws are ubiquitous and actively studied in many scientific fields, including the plasticity of materials. We first performed large-scale molecular dynamics (MD) simulation and nano-indentation testing, and then reported the power law statistics in the second and subsequent pop-in (displacement burst) during the load-controlled nano-indentation test [1]. The first pop-in was characterized by Gaussian-like statistics with a well-defined average value. The transition from Gaussian-like to a power law is because of the change in the deformation mechanism from dislocation nucleation to dislocation network evolution in the sharp-indenter-induced abruptly decaying stress and dislocation density fields.

The nano-indentation tests on the (100) and (111) surfaces of body-centered cubic (BCC) iron showed that the scaling exponents of the power laws were 5.6 and 3.9, respectively. These power law exponents are much higher than those typically observed in micropillar plasticity (1.0 - 1.8), suggesting that the nano-indentation plasticity belongs to a different universality class than micropillar plasticity.

Figure 1 shows the large-scale molecular dynamics nano-indentation simulation results for the first pop-in, and the subsequent pop-in observed in the nano-indentation simulation on the Fe (100) surface. Dislocation nucleation, dislocation network activities, and the corresponding stress-field change, which are the origins of the high power-law exponent, were clearly simulated. Figure 2 shows the power-law statistics of the subsequent pop-in magnitude obtained by MD and actual nano-indentation testing. The MD results reasonably agreed with the experiment. Both MD and experiment showed very high exponents of 5.0 and 5.6, respectively.

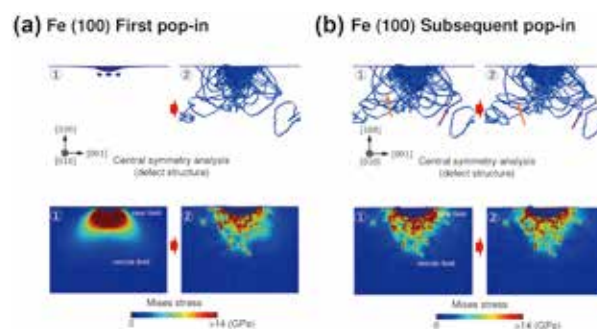


Fig. 1 Molecular dynamics nano-indentation simulation results: (a) first pop-in and (b) subsequent pop-in. The upper panels show dislocation activities. The lower panels show stress field change beneath the indenter tip [1].

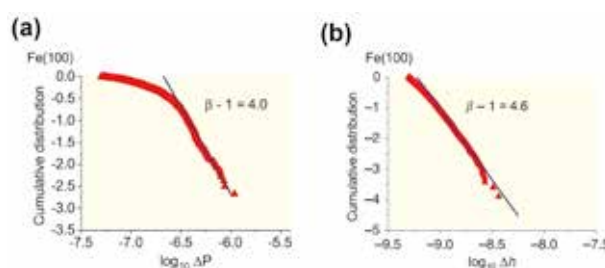


Fig. 2 Power law statistics in nano-indentation pop-ins for BCC Fe(100): (a) MD (load drop) and (b) experiment (displacement burst). β is the power-law exponent [1].

References

- [1] Y. Sato, S. Shinzato, T. Ohmura, T. Hatano, and S. Ogata, *Nature Communications* **11**, 4177 (2020).

Keywords: mechanical properties, molecular dynamics

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Collaborative Research Programs of CNSAM

Center of Neutron Science for Advanced Materials

The Center of Neutron Science for Advanced Materials is a neutron facility with a background in novel materials science at the Institute for Materials Research, Tohoku University. This center manages three neutron instruments in the research reactor facility JRR-3, under a general user program; and a brand new spectrometer POLANO at the Japan Proton Accelerator Research Complex/Materials and Life Science Experimental Facility. In this report, we describe the current status of the research program and the preparations for the restart of JRR-3.

The Center of Neutron Science for Advanced Materials (CNSAM) was established in 2010 to promote novel materials science research using neutrons. CNSAM operates one diffractometer (HERMES) and two neutron spectrometers (TOPAN and AKANE) at the JRR-3 research reactor of the Japan Atomic Energy Agency. HERMES can precisely determine the arrangement of atoms and spins, while their motions are examined by AKANE and TOPAN. These are used for target energy and momentum transfer regimes. POLANO, located at the Materials and Life Science Experimental Facility (MLF) at the Japan Proton Accelerator Research Complex (J-PARC), is a brand new spectrometer designed to perform polarization analysis in higher energy regions beyond those measured by conventional triple-axis spectrometers. POLANO and TOPAN are equipped with polarized options and can disentangle nuclear and magnetic contributions. We aim to contribute to condensed matter physics and materials science with the multipurpose neutron instruments of PATH. Figure 1 shows the PATH, which is a collective term for neutron instruments managed by the CNSAM.

To achieve this purpose, we established an international collaborative research program in IMR from FY 2019. We provide opportunities not only for experiments with neutron beams but also for the development of neutron devices and analysis methods, and even for theoretical work with our neutron data. Proposals can be submitted under several categories, such as “Neutron experiment at MLF,” “Instrumental development,” “Development in analysis method,” “Structural analysis and data handling,” and “Others”. Under the category “Others,” proposals on the complementary use of neutron and other quantum beams, such as X-ray and muon beams, are accepted. In FY 2020, we received 17 and 6 proposals from domestic and overseas researchers, respectively. Despite difficulties in implementing the program this year,



Fig. 1 A photograph of neutron scattering instruments managed by the Center of Neutron Science for Advanced Materials, Tohoku University.

we continue to develop a compact spin-exchange optical pumping system under a collaboration with the High Energy Accelerator Research Organization. This system will be installed in POLANO as a spin filter for high-energy neutrons [1]. Furthermore, as the restart of the JRR-3 is scheduled at the end of FY 2020, we are preparing for the general user program at JRR-3 and checking the operation of the above instruments. We made fact sheets for each instrument, which were broadly distributed to researchers and potential users, and promoted the use of these instruments during online meetings.

References

- [1] T. Okudaira et al., Nucl. Inst. Meth. A **977**, 164301 (2020).

Keywords: neutron diffraction, neutron scattering, instrumentation

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Superconductivity, Quantum Phase Transitions, and Fermi Surface of Strongly Correlated *f*-Electron Systems

International Collaboration Center

We investigated Ir-doped CeRhIn₅, in which quantum criticality occurs at a critical concentration $x_c = 0.6$ by means of the de Haas–van Alphen (dHvA) effect. Our results suggest that the Fermi surfaces (FSs) and effective masses in CeRh_{1-x}Ir_xIn₅ remain unchanged up to at least the critical concentration of Ir. This study will be continued, if necessary, in high magnetic fields up to 36 T at Grenoble. To this end, new samples of CeRh_{1-x}Ir_xIn₅ are being grown.

CeRhIn₅ is among the best-studied heavy fermion (HF) materials. This tetragonal antiferromagnetic (AFM) compound with $T_N = 3.8$ K can be tuned to a quantum critical point (QCP) by pressure, chemical substitution, and magnetic field. The *f* electrons of CeRhIn₅ are localized at ambient pressure. As the critical pressure $P_c = 2.3$ GPa is reached, all dHvA frequencies observed at $P < P_c$ change discontinuously, indicating an abrupt FS reconstruction as a consequence of *f*-electron delocalization.

Another way to tune CeRhIn₅ to quantum criticality is to substitute Rh by Ir [1], as shown in Fig. 1(a). Upon doping CeRhIn₅ with Ir, the antiferromagnetic order is suppressed at the critical concentration $x_c = 0.6$, giving rise to a QCP. Above the Ir concentration of approximately $x=0.3$, a commensurate magnetic order develops and co-exists with the incommensurate structure up to x_c . Finally, superconductivity was observed over a wide concentration range $0.3 < x < 1$. Note that the commensurate AF wave vector was found in 10% Cd-doped CeIrIn₅ in our previous studies [2].

The FSs and effective masses of the end compounds, CeRhIn₅ and CeIrIn₅, are well known. CeRhIn₅ is characterized by FSs with localized *f* electrons and slightly enhanced effective masses. In contrast, CeIrIn₅ has FSs with itinerant *f* electrons and strongly enhanced effective masses. How and where the FSs and effective masses change as a function of Ir concentration is one of the questions that we addressed. To this end, high-quality single CeRh_{1-x}Ir_xIn₅ crystals with different Ir concentrations were grown. Figure 1(b) shows the Fourier spectra of the dHvA oscillations in CeRh_{0.8}Ir_{0.2}In₅ and CeRh_{0.4}Ir_{0.6}In₅. For both compositions, the observed dHvA frequencies and effective masses were the same as in pure CeRhIn₅. This suggests that the FSs and effective masses in CeRh_{1-x}Ir_xIn₅ do not change up to at least the critical concentration of Ir. This finding should, however, be treated with caution, as a more recent microprobe analysis revealed a significant difference between the real and nominal Ir concentrations in some samples. Therefore, new samples of CeRh_{1-x}Ir_xIn₅ are

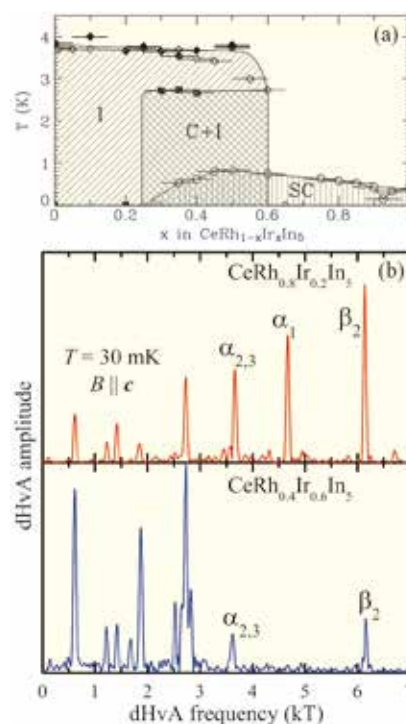


Fig. 1 (a) Temperature-composition phase diagram of CeRh_{1-x}Ir_xIn₅ with three distinct long-range orders: superconducting (SC), incommensurate antiferromagnetic (I), and commensurate antiferromagnetic (C) (adopted from [2]). (b) Fourier spectra of the dHvA oscillations in CeRh_{0.8}Ir_{0.2}In₅ and CeRh_{0.4}Ir_{0.6}In₅.

being grown. All the new crystals will be tested by microprobe and specific heat measurements prior to dHvA studies, and, if necessary, in high magnetic fields up to 36 T at Grenoble.

References

- [1] A. Llobet, A. D. Christianson, W. Bao, J. S. Gardner, I. P. Swainson, J. W. Lynn, J.-M. Mignot, K. Prokes, P. G. Pagliuso, N. O. Moreno, J. L. Sarrao, J. D. Thompson, and A. H. Lacerda, Phys. Rev. Lett. **95**, 217002 (2005).
- [2] K. Beauvois, N. Qureshi, R. Tsunoda, Y. Hirose, R. Settai, D. Aoki, P. Rodière, A. McCollam, and I. Sheikin, Phys. Rev. B **101**, 195146 (2020).

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Dynamical Vortex Phase Diagram of Two-Dimensional Superconductor in Ion-Gated MoS₂

Laboratory of Low Temperature Materials Science

Two-dimensional superconductors with high crystallinity, realized by exfoliation and ionic gating, have revealed various intrinsic properties of quantum vortices. Recently, we found a current-induced phase transition at zero magnetic field in ion-gated MoS₂. This dynamical phase transition can be explained by the appearance of the phase-slip line with Josephson-like ultrafast vortex-antivortex flow.

Two-dimensional (2D) materials with high crystallinity provide ideal platforms to explore the novel phenomena of vortex matter when they become 2D superconductors by exfoliation and ionic gating. While various vortex phases [1] and their dynamics [2] under magnetic fields have been intensively studied in such 2D superconductors, the dynamical properties at zero magnetic field are relatively unexplored. In conventional dirty 2D superconductor films, it is known that the true superconducting state with zero ohmic resistance is achieved at the low-current limit by binding thermally excited vortex and antivortex (V-AV) pairs through the Berezinskii–Kosterlitz–Thouless (BKT) transition. However, the V-AV dynamics beyond the low-current region remains not completely understood, probably because of the effect of disorder on vortices. We dealt with this issue using a gate-induced 2D superconductor, MoS₂, with minimal disorder by measuring the current-voltage (I - V) characteristics [3].

In the low-current region, we obtained the power law behavior $V \propto I^\alpha$ below the mean-field transition temperature $T_{c0} = 7.6$ K, and firm evidence of the BKT transition with the universal jump of α from 1 to 3 at $T_{\text{BKT}} = 6.0$ K, which indicate that our system is a purely 2D superconductor. With increasing I , we found successive step-like increases in $V(I)$ at the characteristic currents I_{c1} , I_{c2} , and I_{c3} ; and in the T -dependence of the nonlinear resistance R_{NL} at T_1 and T_2 , respectively. Eventually, we obtained the I - T dynamical phase diagram shown in Fig. 1. Based on the calculation of the vortex velocity v_f , the anomaly at I_{c1} and T_1 can be considered as the dynamic transition of the V-AV pairs from the BKT state with $v_f \sim 10^3$ m/s (Abrikosov vortex flow) to the ultrafast dynamical state with $v_f \sim 10^5$ to 10^6 m/s (Josephson-like vortex flow).

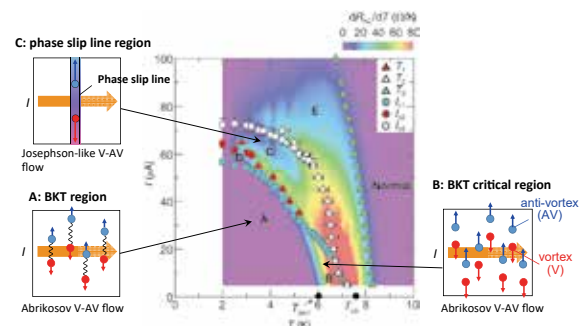


Fig. 1 Current-temperature (I - T) phase diagram of ion-gated MoS₂ at zero magnetic field [3]. Color mapping displays the magnitudes of dR_{NL}/dT . I_{c1} , I_{c2} , and I_{c3} are characteristic currents at which the step-like increase in I - V curves are observed. T_1 and T_2 are the peak temperatures of dR_{NL}/dT . T_3 is the onset temperature of R_{NL} . Schematic images of the flow of vortices and antivortices in region A (BKT region: lower left), region B (BKT critical region: lower right), and region C (phase slip line region: upper left) are shown.

accompanying the phase-slip line across the conducting plane (upper left in Fig. 1). I_3 and T_2 correspond to the transition to the partially normal or fluctuation region. The unexpected richness of the dynamical vortex diagram in Fig. 1 originates from the combination of the weak pinning force, low resistance, and enhanced fluctuations at the 2D limit in our high-crystallinity gated superconductors.

References

- [1] Y. Saito, T. Nojima and Y. Iwasa, Nat. Commun. **9**, 778 (2018).
- [2] Y. M. Itahashi, Y. Saito, T. Ideue, T. Nojima, Y. Iwasa, Phys. Rev. Research **2**, 023127 (2020).
- [3] Y. Saito, Y. M. Itahashi, T. Nojima, Y. Iwasa, Phys. Rev. Mater. **4**, 074003 (2020).

Keywords: superconducting, 2D materials, field-effect transistor

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Research Facility for Physics and Chemistry of Radioactive and Nuclear Materials

Laboratory of Alpha-Ray Emitters

Over 170 species of radioisotopes and nuclear materials are available for study at the Laboratory of Alpha-Ray Emitters. This laboratory is one of the most important centers in the world for studying the physical and chemical properties of radioactive materials, such as actinide compounds. Researchers from many of the leading universities and institutes all over Japan visit this facility every year to prepare a variety of materials and carry out chemical and physical measurements.

The Laboratory of Alpha-Ray Emitters offers a research environment for the study of 170 radionuclides and elements, especially alpha-ray emitters, such as actinide. This lab is a source for pure crystals of actinide compounds, supplying them to other universities and synchrotron orbital radiations. Over the past decade, Actinium-225 (Ac-225) has been provided to other universities and research centers through inter-university collaborations. The radiation-controlled area of this laboratory includes three chemical rooms, three physical rooms, etc., which are equipped with local exhaust ventilation systems that make the handling of various kinds of radioactive materials possible. Many spectrometers, including those for gamma rays and alpha rays, are available.

Ac-225 (half-life: 9.92 d) and Radium-223 (Ra-223, half-life: 11.4 d) are known for their effectiveness in targeted alpha therapy (Fig. 1). Despite the availability of testimonies on the effectiveness of radiopharmaceuticals, very few investigations have been conducted in Japan. One reason is the fact that Ac-225 is subject to rigid regulation as an alpha-ray emitter. On the other hand, Ra-223 chloride salt has been approved in Japan as a drug. To the best of our knowledge, information on the dispersion of both Ac-225 and Ra-223 from an aqueous solution is still rare.

In our laboratory, we developed a special ventilation system for measuring the dispersion of those nuclides and their progeny nuclides (Fig. 2) [1-2]. This evaluation is especially important to establish guidelines for the control standard, especially for useful short-life alpha-ray emitters in practical use. Recently, we evaluated the dispersion of Ac-225 using an alpha-ray spectrometer. To obtain the starting material of Ac-225, we used the Thorium-229 (Th-229) milking method. Th-229 was separated from Uranium-233 stored in our laboratory. The dispersion rate of Ac-225 and its progeny nuclides was well identified. The dispersion rate was obtained in the following order: DOTA complex in neutral > salt in

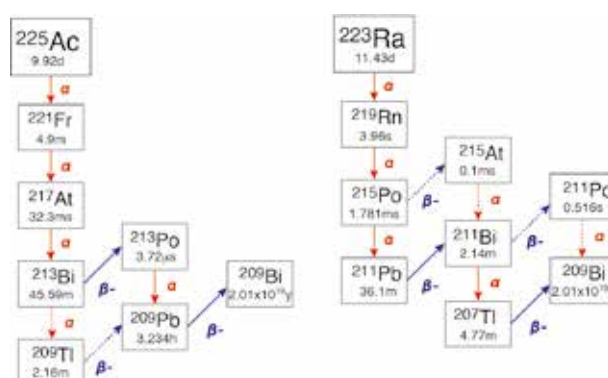


Fig. 1 The decay scheme of Ac-225 and Ra-223.

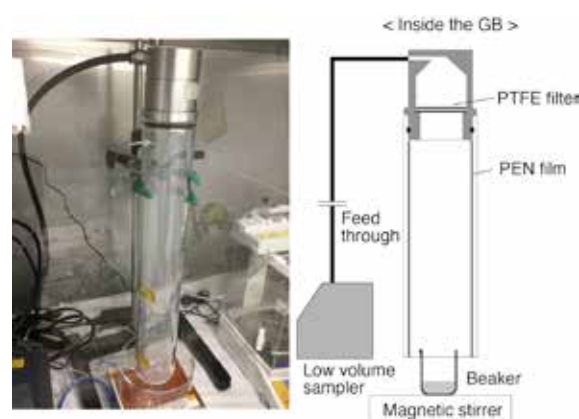


Fig. 2 Special ventilation system for dispersion measurement.

neutral > acidic, in the liquid condition. Even in the highest, the dispersion rate was less than $10^{-4}/\text{h}$, which was 1/100 of the current regulation value.

References

- [1] T. Yamamura, K. Shirasaki, H. Kikunaga, K. Nagata, Zi. J. Zhang, K. Washiyama, A. Toyoshima, T. Yoshimura, and A. Shinohara, Radiation Safety Management. **19**, 35 (2020).
- [2] K. Nagata, K. Shirasaki, A. Toyoshima, K. Ooe, T. Yamamura, A. Shinohara, and T. Yoshimura, Radiation Safety Management **19**, 1 (2020).

Keywords: actinide, alpha-ray spectroscopy

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Direct Observation of Atomic Columns and Identification of Elemental Species in New Layered Perovskite [RbCeTa₂O₇] by Cs-Corrected STEM

Analytical Research Core for Advanced Materials

To examine the crystal structure of a novel Ce-based layered perovskite, RbCeTa₂O₇, the detailed atomic arrangement was observed under a spherical aberration collected by a scanning transmission electron microscope (Cs-corrected STEM). The metallic atom and oxygen columns were identified by energy-dispersive spectroscopy mapping and STEM-annular-bright-field methods, respectively.

Layered perovskite compounds with two-dimensional structures consisting of lanthanide and transition metals exhibit various properties. In particular, Dion–Jacobson and Ruddlesden–Popper-type ion exchangeables have received much attention for photo-functional applications. In this study, we developed a new Ce-included layered perovskite compound RbCeTa₂O₇ [1]. XRD analyses showed that it has a Dion–Jacobson-type layered perovskite structure with the space group of *P4/mmm*, as shown in Fig. 1(a).

For further crystallographic characterization, direct observation of atom columns and identification of the elements occupying each column were carried out using scanning transmission electron microscopy (STEM). The thin film specimen for STEM was prepared by an Ar ion slicer method using resin-filled powder samples. STEM observations were performed at an acceleration voltage of 200 kV using the JEOL JEM-ARM200F equipped with a spherical aberration corrector in both the illuminating and imaging systems. The low magnification observation image in Fig. 1(b) shows that the samples with flake-like morphology were clustered together; hence, a single crystal region without overlap was selected for high-resolution observations. The high-resolution high-angle annular dark field (HAADF) images in Fig. 1(c) show stacked periodic structures with bright contrast. These bright spots correspond to relatively heavy elements: Ta, Ce, and Rb. In contrast, in the annular bright field (ABF) image, lighter elements have bright contrast, as shown in Fig. 1(d); even oxygen columns exhibit gray contrast. Energy-dispersive spectroscopy (EDS) mapping was performed to identify the elemental species in each column consisting of metals and lanthanides, as suggested by HAADF observations. The high-resolution EDS mapping result is shown in Fig. 2.

The STEM results show good agreement with the structural model of the layered perovskite compound RbCeTa₂O₇ based on the x-ray diffraction experiment.

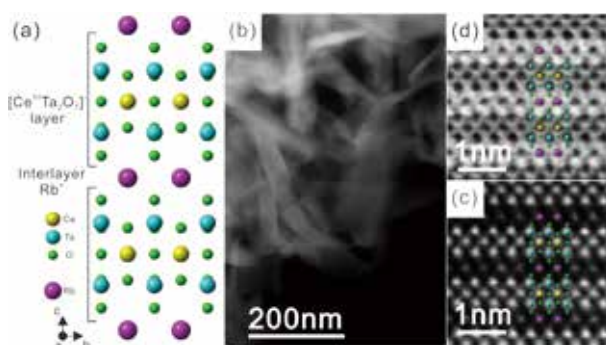


Fig. 1 (a) Schematic drawing of crystal structure of RbCeTa₂O₇, (b) low-magnification, (c) HAADF, and (d) ABF-STEM images of RbCeTa₂O₇.

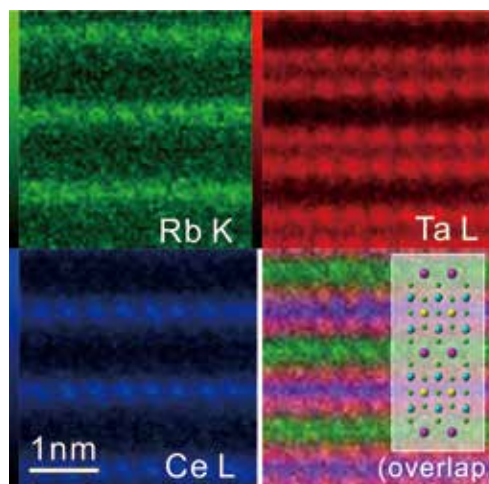


Fig. 2 EDS column mapping of RbCeTa₂O₇. Crystal structure model of RbCeTa₂O₇ (inset).

References

- [1] T. Hasegawa, A. Shigee, Y. Nishiwaki, M. Nagasako, A. T. Hanindriyo, K. Hongo, R. Maezono, T. Ueda, and S. Yin, *Chem. Commun.* **56**, 8591 (2020).

Keywords: electron microscopy, crystal structure

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International Collaborative Research

IMR KINKEN Research Highlights 2021



Toroidal State in {Fe₈Dy₈} Ring Identified by High-Frequency Electron Paramagnetic Resonance

We synthesized a new ring shaped magnet {Fe₈Dy₈} in which the toroidal magnetic state is realized by the cooperation of a strong anisotropy of Dy ion and a substantial ferromagnetic exchange coupling between Dy and Fe ions. The high-frequency electron paramagnetic resonance measurement revealed the ferromagnetic exchange, otherwise the determination is difficult.

In magnetic recording materials, small ferromagnetic particles or ferromagnetic domains with unidirectionally aligned magnetic moments have been used for decades. When the size of the recording approaches the nanoscale, such uniform domain materials show a fundamental vulnerability for weak magnetic fields in the environment. In future societies with advanced electrification, the magnetic fields around us will increase substantially. This highlights the need to develop magnetic recording materials based on a novel concept.

Magnetic molecules are promising candidates for ultra-dense information storage applications. One of the features is the diversity of structures, such as linear, zigzag, star, and ring. Among them, the ring structure shows promise for the possible realization of toroidal magnetic structures. There are two distinguished states in a toroidal structure: the left and right windings. When information is stored as these windings, such states are stable and insensitive to magnetic perturbations. This would be an ideal candidate for nanoscale molecular magnetic storage.

We synthesized a new toroidal magnet called {Fe₈Dy₈}, in which 16 magnetic metal ions can be alternately arranged into a macrocycle [1]. The possibility of the toroidal arrangement is given by the magnetization curve, which shows no spontaneous ferromagnetic moment at zero field, but a slow increase toward higher fields. The magnetization at 7 T was only 40% of the full saturated moment, which indicates two possible arrangements of magnetic moments: ferri-magnetic and toroidal. In the ferrimagnetic case, Dy³⁺ and Fe³⁺ ions were coupled antiferromagnetically, and the strong anisotropy was responsible for the slow increase in magnetization. Note that the easy axis of the anisotropy of Dy³⁺ must rotate in the ring from one Dy³⁺ site to the next, because there is no large spontaneous moment. When a strong magnetic field is applied, the change from the ferrimagnet to ferromagnet will appear in the magnetization curve because the exchange coupling between 4f and 3d ions is often weak.

In the toroidal arrangement, the magnetic moments of both Dy and Fe were aligned along the tangential

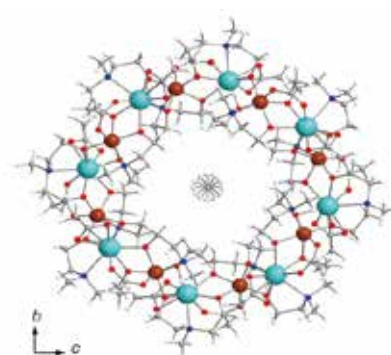


Fig. 1 Structure of {Fe₈Dy₈} molecule. Fe and Dy are represented by large red and sky blue balls. The Dy easy axis is located in the molecular plane.

direction of the ring and were confined in the ring plane owing to the strong anisotropy of Dy ions. The collaboration between ferromagnetic coupling and the strong anisotropy of Dy ions is the key to realizing a toroidal arrangement.

The key experiment distinguishing these two cases is the determination of Dy-Fe exchange coupling by high-frequency electron paramagnetic resonance (EPR) [2]. We observed the systematic frequency-dependence of the EPR spectra at frequencies between 135 GHz and 405 GHz using a THz-ESR system developed by the magnetism division of the Institute for Materials Research, Tohoku University. It shows the linear frequency-field relation with a zero field gap of approximately 110 GHz (5.3 K). The *g*-values determined by the slope of the mode shows that the signal is the transition in the Fe³⁺ multiplet, and the level is exchange-biased by the ferromagnetic coupling between Fe and Dy ions. The total magnetic coupling energy is 26.4 K for one Fe-Dy pair and over 400 K for the whole molecule. The present results provide a useful recipe to design a toroidal magnetic molecule.

References

- [1] H.-L. Zhang, Y.-Q. Zhai, L. Qin, L. Ungur, H. Nojiri, and Y.-Z. Zheng, *Matter* **2**, 1481 (2020).
- [2] H. Nojiri, Y. Ajiro, T. Asano, and J.-P. Boucher, *New J. Phys.* **8**, 218 (2006).

Keywords: high magnetic field, toroidal magnet, electron paramagnetic resonance (EPR)

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Origin of Luminescence in $\text{Y}_2\text{SiO}_5\text{:Ce}$ And $\text{Lu}_2\text{SiO}_5\text{:Ce}$ Single Crystals

We studied the photoluminescence characteristics of Ce^{3+} -doped rare-earth oxyorthosilicates RE_2SiO_5 (RE:Y, Lu) and evaluated the concentrations of different Ce^{3+} -related centers from Electron Paramagnetic Resonance (EPR) spectra. We elucidated the role of Ce^{3+} -related centers in the luminescence of these crystals and proposed a new interpretation of their luminescence spectra.

Ce^{3+} -doped rare-earth (RE) oxyorthosilicates RE_2SiO_5 (RE:Y, Lu) have been extensively studied as promising scintillators. Owing to their high density, short luminescence decay time, high light yield, high stopping power, and good mechanical and chemical properties, single crystals ($\text{Lu,Y})_2\text{SiO}_5\text{:Ce}$ (LSO:Ce and LYSO:Ce) have been employed in detectors in medical imaging, nuclear physics, and several other applications [1]. $\text{Y}_2\text{SiO}_5\text{:Ce}$ (YSO:Ce) possesses comparatively poor scintillation characteristics. However, it has a lower melting point, which is preferable from a technological point of view, and it has been employed in applications such as detectors and imaging screens in high-tech devices.

In their luminescence spectra, the intense violet (V) doublet emission band is located near 3 eV (Ce1 emission) and is ascribed to the allowed $5d \rightarrow 4f$ transitions of the Ce^{3+} ions located at the RE1 site (the Lu1 site in the LSO lattice). A weaker broad blue (B) emission band was observed at approximately 2.75 eV. The origin of the B emission is not yet understood and is usually ascribed to the Ce^{3+} ions at the RE2 site (Ce2 centers) [2].

The investigated high-quality single crystals were grown at Tohoku University [3].

The Ce^{3+} -related emission spectra (Fig. 1) indicate a strong difference in the shapes of the Ce^{3+} -related V and B emission bands. The decomposition of the V emission band results in two doublet bands with significantly different intensities arising from the Ce^{3+} -related centers of two types, Ce1, and Ce2 centers. The decomposition of the B band into three Gaussian components indicates a complex structure of the B band.

Under excitation approximately 3.85 eV, the B and V emission intensities are proportional to the absorption coefficient, and consequently, to the number of the centers responsible for these emission bands. The intensity of the dominant V emission depends linearly on the Ce^{3+} content, which is characteristic for the single Ce^{3+} ions. According to the EPR data, the Ce2 fractional content decreases with increasing Ce^{3+} content. The data obtained indicate that B emission cannot arise from single Ce^{3+} centers.

The detailed analysis of the experimental data on the luminescence and EPR characteristics allows a novel

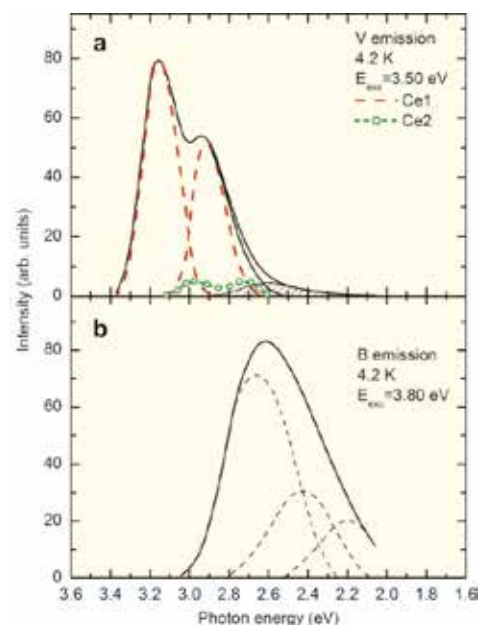


Fig. 1. (a) V emission and (b) B emission spectra and their approximate decomposition into Gaussian components (dashed and dotted lines).

conclusion that is summarized in Ref [4]:

(i) B emission cannot arise from Ce2 centers, as the relative number of these centers and B emission intensity have opposite dependence on Ce^{3+} concentration;

(ii) A considerable difference in the luminescence characteristics of the V and B emissions cannot be explained by different positions (Ce1 and Ce2) of single Ce^{3+} ions;

(iii) The Ce1 and Ce2 centers in LSO:Ce and YSO:Ce should have similar luminescence characteristics.

References

- [1] C.L. Melcher and J.S. Schweitzer, IEEE Trans. Nucl. Sci. **39**, 502 (1992).
- [2] C.L. Melcher, M. Schmand, M. Eriksson, L. Eriksson, M. Casey, R. Nutt, J.L. Lefaucheur, and B. Chai, IEEE Trans. Nucl. Sci. **47**, 965 (2000).
- [3] A. Yoshikawa, M. Nikl, G. Boulon, and T. Fukuda, Opt. Mater. **30**, 6 (2007).
- [4] V. Babin, V.V. Laguta, M. Nikl, J. Pejchal, A. Yoshikawa, and S. Zazubovich, Opt. Mater. **103**, 109832 (2020).

Keywords: scintillator, EPR, luminescence

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Undetectably Low Concentration of Quenched-In Vacancies in High-Entropy Alloys/Mechanical Property Evolution in Beta-Titanium Alloys via Diffusionless Isothermal Omega Transformation

In this report, we introduce two of our research topics: (i) high-entropy alloys (HEAs) and (ii) titanium alloys. Understanding the atomic transport mechanisms in HEAs, including the formation and migration of equilibrium point defects, is essential to clarify their extraordinary properties, such as high irradiation resistance. Positron annihilation lifetime spectroscopy measurements revealed that the concentration of quenched-in thermal vacancies in HEAs with a face-centered cubic structure is as low as below the detection limit (in the order of 10^{-6}). We recently defined the diffusionless isothermal omega (DI- ω) transformation, which gradually proceeds in beta (β)-titanium alloys even at above the ω -transformation temperature. The evolution of mechanical properties, including Vickers hardness, submegahertz internal friction, and elasticity, with the progression of the DI- ω transformation can be explained by the concept of quenched-in thermal concentration fluctuations.

Single-phase solid-solution alloys consisting of multiple principal elements in (nearly) equimolar fractions, often referred to as high-entropy alloys (HEAs), have attracted extensive attention owing to their extraordinary properties, such as high strength, corrosion, and irradiation resistance. Although the formation and migration behavior of vacancies in HEAs is important to understand bulk diffusion and radiation tolerance, there are contradictions between previous reports on the concentration of thermal vacancies in HEAs. Thus, positron annihilation lifetime spectroscopy measurements were conducted to investigate the concentration of thermally induced and quenched-in vacancies in a series of single-phase solid-solution alloys (Cr_{0.3}FeNi_{0.2}, CrFeNi, CoCrFeNi, CoCrFeMnNi, and Al_{0.3}CoCrFeNi) quenched from temperatures close to their melting point as a function of the configurational entropy. The quenched-in vacancy concentration estimated by the mean positron lifetime decreased with the increase in configurational entropy and could fall below the detection limit (in the order of 10^{-6}) of quaternary and quinary alloys [1].

Understanding the ω -transformation mechanism in β -titanium alloys is essential because the ω -phase dominates the microstructure and mechanical properties of titanium alloys. We recently proposed the diffusionless isothermal ω (DI- ω) transformation mode [2], which can gradually occur near room temperature. We investigated variations in the microstructure and mechanical properties of β -Ti-V alloys with the progression of the DI- ω transformation using transmission electron microscopy, differential scanning calorimetry, and measurements of the Vickers hardness, internal friction, and inelastic X-ray

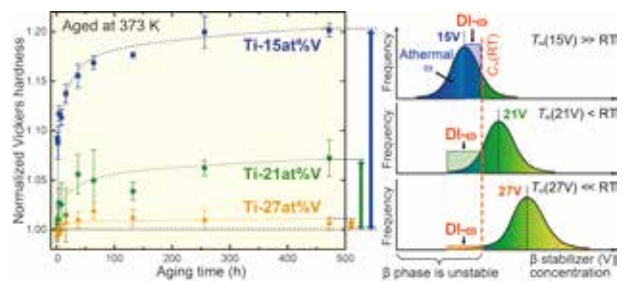


Fig.1. (a) Variation in Vickers hardness as a function of annealing time at 373 K for Ti-15, 21, and 27 at.% V alloys. (b) Schematics of the concentration distribution of the β -stabilizing element (V) for the interpretation of the hardness increase.

scattering [3]. As shown in Fig. 1(a), the Vickers hardness increased with aging at 373 K, where no atomic diffusion occurred. The relative increase in hardness is larger as the vanadium composition is lower. This hardening behavior can be attributed to the DI- ω transformation and interpreted by the concept of the quenched-in concentration distribution of the β -stabilizing element (Fig. 1(b)) [3].

References

- [1] L. Resch, M. Luckabauer, N. Helthuis, N. L. Okamoto, T. Ichitsubo, R. Enzinger, W. Sprengel, and R. Würschum, *Phys. Rev. Materials* **4**, 060601(R) (2020).
- [2] M. Tane, H. Nishiyama, A. Umeda, N. L. Okamoto, K. Inoue, M. Luckabauer, Y. Nagai, T. Sekino, T. Nakano, and T. Ichitsubo, *Phys. Rev. Materials* **3**, 043604 (2019).
- [3] N. L. Okamoto, S. Kasatani, M. Luckabauer, R. Enzinger, S. Tsutsui, M. Tane, and T. Ichitsubo, *Phys. Rev. Materials* **4**, 123603 (2020).

Keywords: high entropy alloy, vacancy, phase transformation

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Strong Antiferromagnetic Coupling of Cobalt(II)–Semiquinone Radical in a Dinuclear Complex with 2,2′-Bipyrimidine Ligands

In this study, a new dinuclear cobalt(II)–radical complex $[\text{Co}_2(3,5\text{-DBSQ})_4(\text{bpym})] \cdot (3,5\text{-DBCatH}_2)_4$ (**1**) (3,5-DBSQ = 3,5-di-*tert*-butylsemiquinone, 3,5-DBCatH₂ = 3,5-di-*tert*-butylcatecholato, bpym = 2,2′-bipyrimidine) was synthesized and characterized using single-crystal X-ray crystallography. Simulated results indicated relatively strong antiferromagnetic exchange coupling between cobalt(II) centers and semiquinone radical ligands.

The combination of organic radicals with metal ions has received considerable attention in the field of molecular magnetism owing to the construction of various molecular magnetic materials. Among molecular magnetic materials, complexes containing semiquinone radicals have become the focus because of their ease of chemical modification, diverse coordination structures, and various properties. Among all the transition metal complexes with the semiquinone ligand, cobalt complexes have been extensively investigated because of their interesting behavior in the presence of a magnetic field.

Here, dinuclear cobalt(II) complexes with a 2,2′-bipyrimidine bridging ligand $[\text{Co}_2(3,5\text{-DBSQ})_4(\text{bpym})](3,5\text{-DBCatH}_2)_4$ were synthesized, and their single-crystal structures were characterized by single-crystal X-ray diffraction [1]. The multidentate ligand, 2,2′-bipyrimidine (bpym), is a bis(α -diimine)-type ligand that can exhibit single chelating and bis-chelating coordination modes in its metal complexes. The organic radical ligand, 3,5-DBSQ, can act as a terminal radical ligand to couple with metal ions and form an almost symmetric binuclear cobalt(II)–radical complex.

Plots showing the magnetic properties of the dinuclear complex with respect to the magnetic susceptibility ($\chi_M T$ vs. T) were obtained between 1.8 and 400 K under an applied field of 1000 Oe. Upon cooling, the value of $\chi_M T$ continuously and rapidly decreased. The experimental susceptibility (10–400 K) was fitted using the PHI program to determine the nature and magnitude of the spin Hamiltonian parameters. Thus, Eq. 1 and Eq. 2 are the Hamiltonians used to fit the experimental magnetic data.

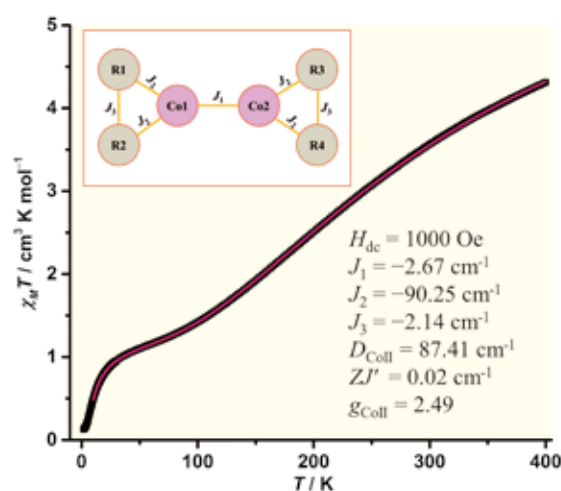


Fig. 1 Experimental $\chi_M T$ vs. T plot for **1** and the best-fit result (red line) using the PHI.

$$\hat{H} = -2J_1(S_{\text{Co1}}S_{\text{Co2}}) - 2J_2(S_{\text{Co1}}S_{\text{R1}} + S_{\text{Co1}}S_{\text{R2}} + S_{\text{Co2}}S_{\text{R3}} + S_{\text{Co2}}S_{\text{R4}}) - 2J_3(S_{\text{R1}}S_{\text{R2}} + S_{\text{R3}}S_{\text{R4}}) + D(S^2_{\text{Co1z}} + S^2_{\text{Co2z}}) + g\beta H \cdot (S_{\text{Co1}} + S_{\text{Co2}}). \quad (1)$$

$$\chi_M = \frac{\chi_{\text{fit}}}{1 - (2zJ' / Ng^2\beta^2)\chi_{\text{fit}}} \quad (2)$$

The fitting procedure extracted the fitted values of $J_1 = -2.67 (\pm 0.004) \text{ cm}^{-1}$, $J_2 = -90.25 (\pm 0.023) \text{ cm}^{-1}$ and $J_3 = -2.14 (\pm 0.36) \text{ cm}^{-1}$ with $D_{\text{Coll}} = 87.41 (\pm 0.23) \text{ cm}^{-1}$, $g_{\text{Coll}} = 2.49 (\pm 0.0002)$, and $zJ' = 0.02 (\pm 0.005) \text{ cm}^{-1}$ (by fixing $g_R = 2.0$, $R = 1.85 \times 10^{-4}$) (Fig. 1). The large negative value of J_2 indicated relatively strong antiferromagnetic properties between the Co(II) ions and semiquinone radical ligands.

References

- [1] J. H. Wang, J. W. Dai, Z. Y. Li, and M. Yamashita, *New J. Chem.* **44**, 8471 (2020).

Keywords: magnetic properties, antiferromagnets, crystal structure

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Effect of the Synthesis Conditions of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ Powder on its Morphology and Characteristics of the Oxygen Ion-Conducting Ceramics Obtained by Spark Plasma Sintering

In this work, two 10 mol.% Gd-doped ceria powders were obtained by thermal decomposition of the same plate-like oxalate precursor under different reaction conditions. The powders with different morphologies were sintered using spark plasma sintering. Electron microscopy was applied to investigate the ceramic samples obtained; their ionic conductivities were measured and compared.

The material 10 mol.% Gd-doped ceria (10GDC) is widely used as a solid electrolyte in solid oxide fuel cells (SOFC). The high oxygen conductivity of 10GDC at intermediate temperatures 500–700 °C is ideal for use in SOFCs. However, ceria powders usually have poor sinterability that complicates the manufacturing of materials. To improve the sintering of the powder, one can change its morphology or/and use nonconventional methods for sintering, such as spark plasma sintering (SPS). In this work, 10GDC powders were obtained by thermal decomposition of the plate-like oxalate precursor $\text{Ce}_{1.8}\text{Gd}_{0.2}(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. This work aims to investigate the influence of the thermal decomposition conditions on the 10GDC morphology and the properties of the ceramics sintered by SPS.

The main factor that influenced the morphology was found to be water vapor pressure during the dehydration stage at 125 °C. Upon dehydration with a fast water removal rate, the crystal retained its shape and size (pseudomorph, termed as "pseudo"), forming an X-ray amorphous product (Fig.1a). Slow dehydration implemented under an elevated water vapor pressure (Quasi-Equilibrium conditions, termed as "QE") led to the intensive shattering of initial crystals and the formation of a crystalline intermediate product (Fig.1b). The observed morphological changes reflected two different topotaxial transformations. These transformations were characterized by different deformation patterns of the crystal structure, causing significant differences in the morphology evolution during dehydration.

Following the oxidation of the two dehydrated products in air at 300 °C, the 10GDC-pseudo and 10GDC-QE powders were obtained with no further significant morphological changes. Crystallite sizes calculated from the X-ray diffraction peak broadening were approximately 5–6 nm in each case, which correlated with the transmission electron microscopy data obtained using the JEM 2010 microscope. The sizes and shapes of the nanoparticle agglomerates were tailored at the dehydration stage. The specific surface area and pore volume of the powders were measured by ASAP 2020.

The 10GDC powders were compacted and sintered using

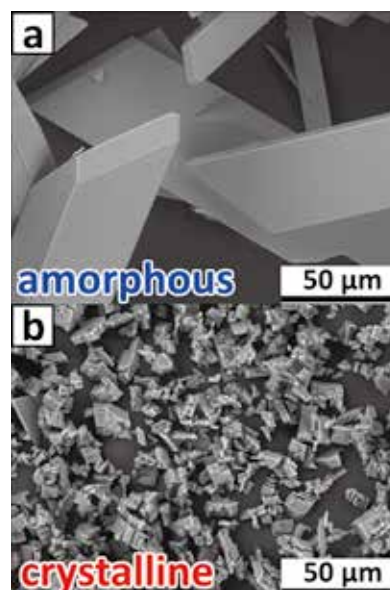


Fig. 1 Morphology of the air dehydrated product (a) and the product obtained by dehydration under an elevated water vapor pressure (b)

SPS under identical conditions. Then, the samples were annealed in air at 1200 °C to oxidize them and eliminate the rest of carbon. The obtained ceramics were investigated by an ULTRA 55 microscope. Unlike the 10GDC-pseudo sample, the 10GDC-QE sample obtained from the precursor dehydrated under high vapor pressure had no visible fractures and showed a higher relative density. This sample also had higher ionic conductivity (2.07 S/m vs. 0.27 S/m at 700 °C) and lower activation energy (66 kJ/mol vs. 85 kJ/mol).

Thus, the dehydration conditions of the chosen precursor were found to be an essential factor in controlling the morphology of 10GDC powder. Changing the powder morphology yielded ceramics with various characteristics [1].

References

- [1] D.V. Maslennikov, A.A. Matvienko, A.A. Sidelnikov, D.V. Dudina, M.A. Esikov, R.V. Belosludov, and H. Kato, *Ceramics International* **47**, 2557 (2021).

Keywords: sintering, oxide, ionic conductor

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Anisotropy of the Upper Critical Field Under Pressure in the Heavy Fermion Superconductor UTe₂

International Research Center for Nuclear Materials Science

We studied the anisotropy of the superconducting upper critical field H_{c2} under pressure in UTe₂ in the spin-triplet state. The superconductivity collapsed at 1.5 GPa, and a magnetically ordered state appeared. The H_{c2} curve for the field along the a -axis showed an abrupt enhancement at the high-field and low-temperature regions, implying different order parameters. The H_{c2} curve for the b -axis showed the cutoff of superconducting phases above the metamagnetic transition field $H_m \sim 35$ T at ambient pressure with the field-reentrant behavior, which was immediately suppressed with pressure. Our results demonstrate the novel interplay between spin-triplet superconductivity and magnetism.

The recent discovery of superconductivity in the heavy fermion paramagnet UTe₂ has attracted much attention because of its novel phenomena. The superconducting state below $T_c = 1.6$ K is proposed to be a spin-triplet state, as it is established in ferromagnetic superconductors, such as URhGe and UCoGe. In UTe₂, a field-robust superconductivity, which significantly exceeds the Pauli limit, was observed at the verge of the ferromagnetic order. Thus, the spin-triplet state is most likely to be realized.

We measured the magnetoresistance under pressure for the field along the a -, b -, and c -axes in the orthorhombic structure of UTe₂ [1]. The measurements were performed in Oarai, Sendai, and Grenoble within the framework of an international collaboration project between IMR and UGA/CEA-Grenoble. Figure 1 shows the H - T phase diagram of H_{c2} at different pressures for $H \parallel a$ and b -axes. For the $H \parallel a$ -axis corresponding to the easy-magnetization axis, an unusual enhancement was detected at low temperature and in the high-field region at 0.5 and 0.86 GPa. At a higher pressure (1.4 GPa), the initial slope of H_{c2} was almost vertical or even positive, indicating that superconductivity was stabilized by the magnetic field. For the $H \parallel b$ -axis, the field-reentrant superconductivity was suppressed owing to the suppression of the metamagnetic transition field H_m . At 1.32 GPa, the H_{c2} curve showed a strong convex curvature, and $H_{c2}(0)$ was reduced to 9 T, which is approximately equal to H_m .

These typical H_{c2} curves under pressure for the a and b -axes were attributed to the multiple superconducting phases originating from the spin degree-of-freedom for the spin-triplet state. The multiple superconducting phases were experimentally detected as a thermodynamic response [2], indicating different order parameters. Another important factor is the interplay with magnetism, which developed above 1.5 GPa in a long-range order. The Fermi surface reconstruction induced by a magnetic field and pressure, such as the Lifshitz transition [3], will play an important role in spectacular superconducting phases.

This work was done in collaboration with G. Knebel, K. Motoi, M. Valiska, F. Honda, D.X. Li, D. Braithwaite, G. Lapertot,

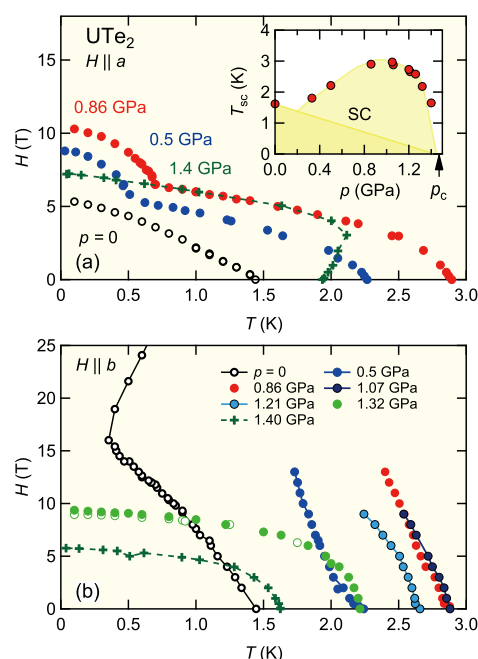


Fig.1: Upper critical field H_{c2} for the field along a and b -axes at different pressure in UTe₂ [1]. The inset of panel (a) show the T - P phase diagram at zero field.

W. Knafo, A. Pourret, Y. J. Sato, Y. Shimizu, T. Kihara, J. P. Brison, and J. Flouquet.

References

- [1] G. Knebel, K. Motoi, M. Valiska, F. Honda, D.X. Li, D. Braithwaite, G. Lapertot, W. Knafo, A. Pourret, Y. J. Sato, Y. Shimizu, T. Kihara, J. P. Brison, J. Flouquet, and D. Aoki, J. Phys. Soc. Jpn. **89**, 053707 (2020).
- [2] D. Aoki, F. Honda, G. Knebel, D. Braithwaite, A. Nakamura, D.X. Li, Y. Homma, Y. Shimizu, Y. J. Sato, J. P. Brison, and J. Flouquet, J. Phys. Soc. Jpn. **89**, 053705 (2020).
- [3] Q. Niu, G. Knebel, D. Braithwaite, D. Aoki, G. Lapertot, M. Valiska, G. Seyfarth, W. Knafo, T. Helm, J. P. Brison, J. Flouquet, and A. Pourret, Phys. Rev. Res. **2**, 033179 (2020).

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Evaluation of Electromechanical Properties in Practical REBCO Coated Conductor Tapes Under Magnetic Field for Superconducting CC Coils

High Field Laboratory for Superconducting Materials

Mechanical and electromechanical properties of practical REBCO CC tapes were evaluated, and were found to vary as the test temperature decreased from 77 K to 35 K. Each CC tape showed a significant increase in elastic modulus, yield strength, and irreversible stress limit as a result of a hardening effect at low temperature. All practical CC tape samples evaluated are suitable for the expected operating conditions in a large-scale superconducting wind power generator, given that all exceeded the critical values required for the irreversible strain limit ($\sim 0.4\%$).

The electromechanical properties of various CC tapes were evaluated at 77 K and self-field; and 35 K and 2 T, as shown in Fig. 1(a) and (b), respectively. The I_c decreased gradually, showing a strain-sensitive behavior at 77 K and a self-field condition, as seen in Fig. 1(a). The strain sensitivity was slightly different depending on the fabrication process adopted, and the alignment direction of the grains on the REBCO layer to the loading axis influenced its sensitivity. At 35 K and 2 T, I_c was almost uniform across all samples before gradually decreasing. This is the result of decreased strain sensitivity in I_c at low test temperatures and an increasing externally applied magnetic field. At 35 K, although I_c remained nearly flat against either the applied strain or stress, it suddenly decreased when its critical value was exceeded. Fig. 1(b) shows that although I_c decreased by 10% to 20% under the applied strain, it recovered when the applied load

was removed.

The electromechanical properties of all CC tape samples are shown in [1]. All samples showed increased irreversible stress limits when the test temperature decreased from 77 K to 35 K. The ISD/RCE sample showed larger irreversible limits at 35 K and 2 T ($\epsilon_{irr} = 0.44\%$; $\sigma_{irr} = 655$ MPa) than at 77 K and self-field ($\epsilon_{irr} = 0.30\%$; $\sigma_{irr} = 370$ MPa). The opposite was true for the other two samples. Both showed lower limits for ϵ_{irr} at 35 K and 2 T (0.60% for RCE-DR and 0.30% for PLD) than at 77 K and self-field.

Among the three practical CC tape samples tested, RCE-DR showed a superior irreversible strain limit of $\epsilon_{irr} = 0.60\%$ at 35 K and 2 T.

References

- [1] H. S. Shin, M. A. Diaz, M. Velasco, and S. Awaji, IEEE Trans. Appl. Supercond. **30**, 8400405 (2020).

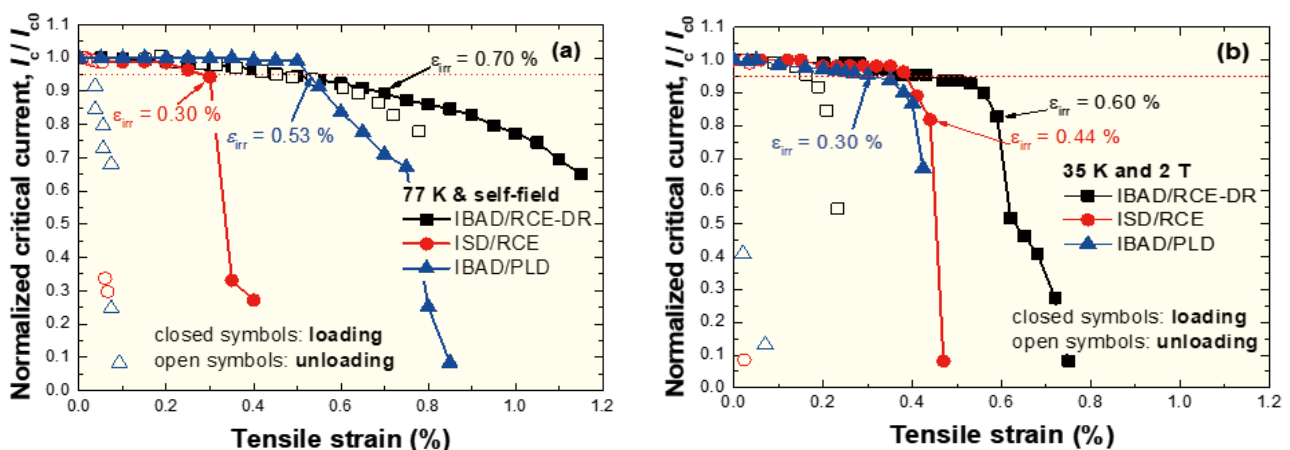


Fig. 1 Normalized critical current as a function of tensile strain at (a) 77 K and self-field, and (b) 35 K and 2T.

Keywords: high temperature superconductor, mechanical properties, high magnetic field

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Ultimate Impedance of Coherent Heat Conduction in Van Der Waals Graphene-MoS₂ Heterostructures

Center for Computational Materials Science

Herein, we investigate the controllability of coherent phonon transport in van der Waals graphene-MoS₂ heterostructures with different stacking orders using molecular dynamics simulations. Using Bayesian optimization-based materials informatics, the optimal stacking order of graphene and MoS₂ was identified from tens of thousands of candidates with varying degrees of phonon localization.

There are growing efforts to control thermal transport via coherent phonons in the one-dimensional superlattice. However, the difference between the intrinsic lattice structures of constituent materials generate interface disorders during the fabrication process, hindering the direct experimental observation of coherent phonon transport. The flexible integration and atomistic interlayer smoothness of the van der Waals heterostructure provides an ideal platform for coherent phonon transport manipulation. Thus, in the current work, non-equilibrium molecular dynamics simulations were used to investigate the coherent phonon transport in a van der Waals graphene-MoS₂ heterostructure with different stacking orders [1]. The histogram of phonon transmissions in different disordered structures exhibits a log-normal distribution, which reveals the localization of coherent phonons. The optimal stacking order of the graphene and MoS₂ was efficiently identified from tens of thousands of candidates by machine learning. The suppression of phonon transmission in the low-frequency (<5 THz) phonons of the optimized structure led to a significant reduction (>95%) of the thermal conductance compared with pristine graphite. Finally, the effects of the defect, size, and temperature on the thermal conductivity of graphite and optimized structures were discussed. Our work provides deep insights into coherent phonons transport behavior in the atomistically smooth van der Waals structure, which is beneficial for the further development of phononics.

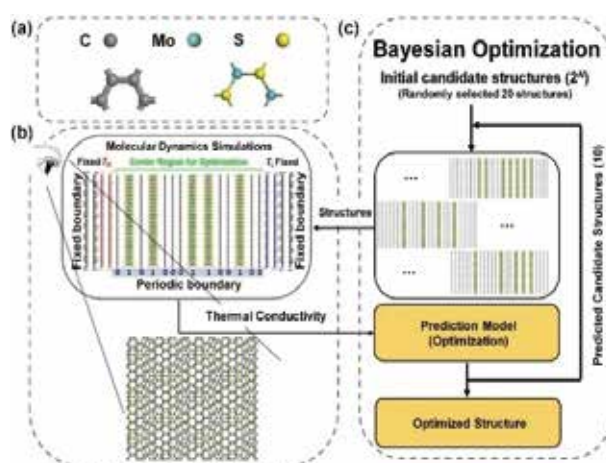


Fig. 1. Schematics of the machine learning method to combine molecular dynamics and Bayesian optimization.

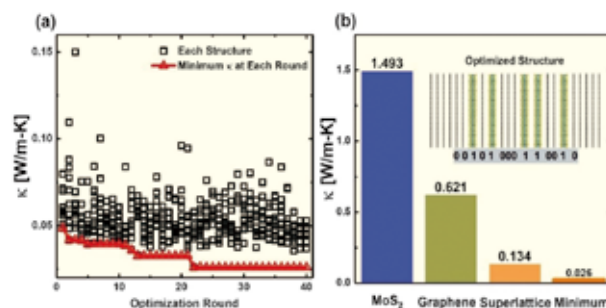


Fig. 2. Comparison of the thermal conductivity between pristine MoS₂, graphene, MoS₂-graphene superlattice, and optimum heterostructure.

References

- [1] S. Hu, S. Ju, C. Shao, J. Guo, B. Xu, M. Ohnishi, and J. Shiomi, *Mater. Today Phys.* **16**, 100324 (2021).

Keywords: 2D materials, molecular dynamics, nanostructure

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Observation of Magnetic Excitation in a Quantum Spin System at POLANO

Center of Neutron Science for Advanced Materials

The neutron spectrometer POLANO at J-PARC is a powerful instrument that will enable polarization analysis in higher energy regions up to 100 meV to elucidate the detailed spin and lattice dynamics. Utilizing POLANO, we measured the phonon density of states in the T*-type cuprate superconductor $\text{Nd}_{1.34}\text{Ce}_{0.26}\text{Sr}_{0.4}\text{CuO}_4$ and clarified the negligible oxidation annealing effect on high-energy bond-stretching phonon.

The interplay between spin, charge, and lattice dynamics is an important subject in the research on high-transition-temperature superconductivity in cuprate oxides [1]. Recently, we synthesized T*-type cuprate, which contains a CuO_5 pyramid in the unit cell, and determined a phase diagram for as-sintered and oxidation annealed samples. Superconductivity in T*-type cuprate appeared after the suppression of the short-range magnetic order due to annealing. Thus, phonon modes could be varied by carrier doping [2] and introducing oxygen brought by annealing. To elucidate the phonon variations and their relation to superconductivity, we performed inelastic neutron scattering measurements on the chopper spectrometer POLANO, which was recently supplied for a user program at MLF.

Figures 1(a) and (b) show the neutron scattering intensity (I) in the energy (E) and momentum (Q) spaces of as-sintered and annealed polycrystal samples of $\text{Nd}_{1.34}\text{Ce}_{0.26}\text{Sr}_{0.4}\text{CuO}_4$, respectively. The intensity was obtained after subtracting the background and multiplying it by E^2 to enhance the I at the higher E region. In both samples, the optical phonon corresponding to the bond-stretching mode in the CuO_2 plane was approximately 100 meV. Figure 1(c) shows the constant- Q spectra at $Q = 7.5 \text{ \AA}^{-1}$. The peak position of the optical phonon is almost the same for the two samples, indicating the negligible annealing effect on this phonon mode. This result contrasts with the softening of optical phonons due to carrier doping in T-type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, which has a CuO_6 octahedron in the unit cell. These results show that phonon softening develops differently in T*- and T-type cuprates.

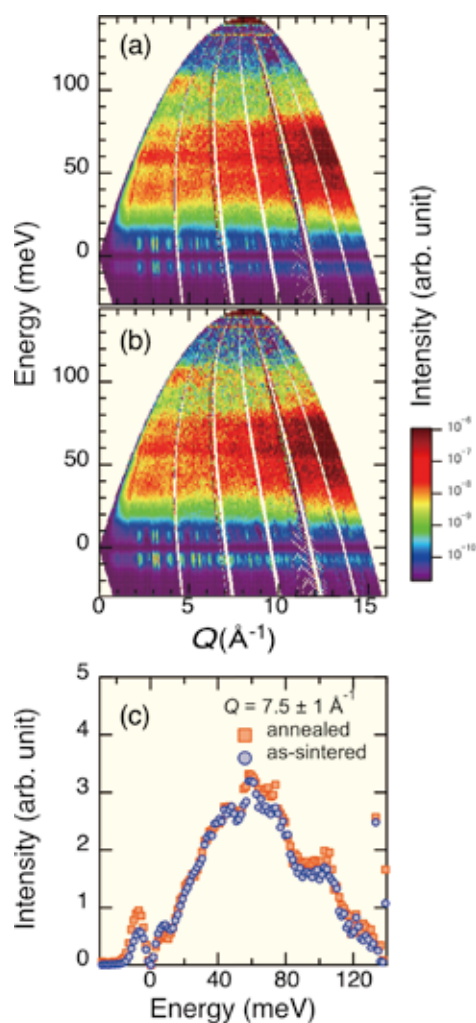


Fig. 1. Neutron scattering intensity for (a) as-sintered and (b) annealed T*-type $\text{Nd}_{1.34}\text{Ce}_{0.26}\text{Sr}_{0.4}\text{CuO}_4$. (c) Constant- Q spectra at $Q = 7.5 \text{ \AA}^{-1}$.

References

- [1] S. Asano, K. Ishii, K. Yamagami, J. Miyawaki, Y. Harada, and M. Fujita, *J. Phys. Soc. Jpn.* **89**, 075002 (2020).
- [2] K. Sato, K. Ikeuchi, R. Kajimoto, S. Wakimoto, M. Arai, and M. Fujita, *J. Phys. Soc. Jpn.* **89**, 114703 (2020).

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Research Highlights
2021

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